RECOMMENDED GUIDELINES FOR MEASURING METALS IN PUGET SOUND MARINE WATER, SEDIMENT AND TISSUE SAMPLES

Prepared for

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LIST OF ACRONYMS

AA	ATOMIC ABSORPTION
ACS	AMERICAN CHEMICAL SOCIETY
APDC	AMMONIUM PYROLIDINE DITHIOCARBAMATE
APHA	AMERICAN PUBLIC HEALTH ASSOCIATION
AR	ANALYTICAL REAGENT (GRADE)
ASTM	AMERICAN SOCIETY FOR TESTING AND MATERIALS
AVS	ACID VOLATILE SULFIDE
CCB	CONTINUING CALIBRATION BLANK
CCV	CONTINUING CALIBRATION VERIFICATION
CFR	CODE OF FEDERAL REGULATIONS
CRM	CERTIFIED REFERENCE MATERIAL
CSL	CLEANUP SCREENING LEVEL
CV	COEFFICIENT OF VARIATION
CVAA	COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY
CVAF	COLD VAPOR ATOMIC FLUORESCENCE
EMMC	ENVIRONMENTAL METHODS MANAGEMENT COUNCIL
EPA	UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
FLAA	FLAME ATOMIC ABSORPTION SPECTROSCOPY
GFAA	GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY
8-HOQ	8-HYDROXYQUINOLINE
ICB	INITIAL CALIBRATION BLANK
ICP-OES	INDUCTIVELY COUPLED ARGON PLASMA SPECTROMETRY/OPTICAL EMISSION SPECTROSCOPY
ICP-MS	INDUCTIVELY COUPLED ARGON PLASMA SPECTROMETRY/MASS SPECTROMETRY
ICS	INTERFERENCE CHECK SAMPLE
ICSA	INTERFERENCE CHECK SAMPLE SOLUTION A
ICSAB	INTERFERENCE CHECK SAMPLE SOLUTION AB
ICV	INITIAL CALIBRATION VERIFICATION
IDA	IMINODIACETATE
IEC	INTERELEMENT CORRECTION
IRIS	INTEGRATED RISK INFORMATION SYSTEM
LCS	LABORATORY CHECK SAMPLE
LD	LABORATORY DUPLICATE
MB	METHOD BLANK
MCUL	MINIMUM CLEANUP LEVEL
MDL	METHOD DETECTION LIMIT
MS	MATRIX SPIKE
MSD	MATRIX SPIKE DUPLICATE
NIST	NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
NOAA	NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
NRCC	NATIONAL RESEARCH COUNCIL OF CANADA
NTR	NATIONAL TOXICS RULE
PPT	PRECIPITATION
PSAMP	PUGET SOUND AMBIENT MONITORING PROGRAM
PSDDA	PUGET SOUND DREDGED DISPOSAL ANALYSIS
PSEP	PUGET SOUND ESTUARY PROGRAM
PSP&G	PUGET SOUND PROTOCOLS AND GUIDELINES

LIST OF ACRONYMS (CONTINUED)

PSWQA	PUGET SOUND WATER QUALITY AUTHORITY
PSWQAT	PUGET SOUND WATER QUALITY ACTION TEAM (FORMERLY PSWQA)
PTFE	POLY(TETRAFLUOROETHYLENE)
QA	QUALITY ASSURANCE
QC	QUALITY CONTROL
RPD	RELATIVE PERCENT DIFFERENCE
RSD	RELATIVE STANDARD DEVIATION
SAD	STRONG ACID DIGESTION
SB	SPIKE BLANK
SDA	SPIKE DUPLICATE ANALYSIS
SEM	SIMULTANEOUSLY EXTRACTED METALS
SMS	SEDIMENT MANAGEMENT STANDARDS
SQS	SEDIMENT QUALITY STANDARDS
SRM	STANDARD REFERENCE MATERIAL
SW-846	EPA TEST METHODS FOR EVALUATING SOLID WASTE (SW-846 3RD EDITION)
TAD	TOTAL ACID DIGESTION
WER	WATER EFFECT RATIO
WQC	WATER QUALITY CRITERIA

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Cheryl Kamera and Dana Walker of the King County Environmental Laboratory were the project managers. Dr. John Armstrong of the United States Environmental Protection Agency (EPA) and Dr. Timothy Ransom (PSWQAT) were the project monitors.

1. INTRODUCTION

The purpose of developing these guidelines is to encourage all Puget Sound investigators conducting monitoring programs, baseline surveys and intensive environmental investigations to use standard methods wherever possible. If this goal is achieved, most data collected for Puget Sound should be directly comparable and thereby capable of being integrated into a Sound-wide database. Such a database is necessary for developing and maintaining a comprehensive water quality management program for Puget Sound. This document presents guidelines for measuring metals in marine water, sediment, and tissue samples from Puget Sound.

From surveys, workshops, and personal interviews conducted over the past 2 years, the original Metals Chapter of the Puget Sound Protocols and Guidelines [PSP&G; (PSEP, 1989)] has been revised to reflect current practices and recommendations of the primary investigators who provide data for the regional databases. These guidelines were revised with the assistance of representatives from organizations that fund or conduct environmental studies in the Puget Sound region (Table 1).

Thorough project planning is also essential, due to the inherent complexity of sampling and analysis activities. The presence of multiple programs and activities in the Puget Sound region further enhances the need for project planning. This chapter should be used in conjunction with the *Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound* and the *Recommended Quality Assurance and Quality Control Guidelines for the Collection of Environmental Data in Puget Sound*. These two chapters are referred to throughout this document as the Field Chapter (PSEP, 1997a) and Quality Assurance (QA) Chapter (PSEP, 1997b), respectively.

Although the following methods are recommended for most studies conducted in Puget Sound, departures from these recommendations may be necessary to meet the special requirements of individual projects. If such departures are made, however, the funding agency or investigator should be aware that the resulting data may not be compatible with other data. In some instances, data collected using different methods have been inappropriately combined in the past. In other instances, when the methods were adequately intercalibrated, data have been combined appropriately. The use of standardized methodologies should aid in producing data of definable quality, enhancing our ability to combine and compare data sets.

Table 1
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2. GENERAL CONSIDERATIONS

2.1 Data Quality Objectives

A formal planning process, as described in Section 2 of the QA Chapter (PSEP, 1997b), is used to ensure that project data support project objectives. During this planning process, analytical methods and other related activities are specified. These decisions are based on the data quality objectives, which are developed after the project objectives and expected use of the data are clarified. Section 2.4 of the QA Chapter (PSEP, 1997b) offers guidance regarding how to develop data quality objectives for a specific project. To best ensure that data quality objectives for a project are met, the laboratory performing the analyses must be involved in the development of the project planning document and must understand the project requirements in advance of receiving samples.

2.2 Contamination and Low Level Work

Sample contamination directly affects the laboratory's ability to analyze a sample accurately at low concentrations. Every precaution should be taken to avoid contamination at each stage of sample collection, handling, storage, preparation and analysis. Much of the historical data for ambient waters reflect contamination from sampling and analysis rather than ambient levels (EPA, 1994a). The majority of trace metals analyses performed in support of Puget Sound Programs require low detection limits, making contamination control an essential factor in trace metals work. The following guidance is intended to provide assistance in minimizing metals contamination and should be followed, as needed, to meet project required detection limits.

It is advisable that laboratories generating trace level data conduct trace level work on an ongoing basis so that procedures and facilities are proven. The laboratory's quality control (QC) program should contain QC samples such as method blanks, glassware blanks and equipment blanks that allow for continually updated knowledge regarding background levels in the sample processing environment. The laboratory's QC program should address the matter of assessing contamination, identifying sources of contamination and eliminating or minimizing those sources of contamination. In addition, sample collection methods and the field QC program must be equally rigorous to ensure that the samples are not contaminated during the sampling or transport processes.

The best way to control contamination in the laboratory is to completely avoid exposure to contamination by performing operations in an area known to be free from contamination (EPA, 1995a); a clean environment should be used for processing low level samples. Performing low level work in a clean room or a clean, nonmetal, laminar flow fumehood will help to minimize problems resulting from metals contamination. Admittance to clean areas should be restricted and personnel should be trained in clean sample handling techniques. It is recommended to dedicate the clean areas to trace level work and isolate samples with high concentrations of metals to other areas. EPA document 821-B-95-0 *Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities* April 1995, Draft (EPA, 1995a) provides more in-depth information on clean room design. EPA Method 1669: *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (EPA, 1995b) discusses "clean" and "ultraclean" techniques and detailed methods for preventing contamination during sampling.

Procedures should be performed by well-trained, experienced personnel who pay strict attention to the work being done. Physical sample handling should be kept to a minimum. Exposure of samples and labware to airborne dust should be minimized during sampling and analysis.

Field equipment and labware must be carefully cleaned and cleaning methods must be monitored and verified using field and laboratory blanks. The time between cleaning and use of labware should be kept to a minimum. Labware should be enclosed in polyethylene zip-locked bags for storage or stored in a dilute nitric acid bath until time of use. Labware with tops, such as bottles and volumetric flasks can be filled with dilute nitric acid, closed and stored upright with the nitric acid until time of use. Apparatus can be covered with clean plastic wrap and stored in a clean area.

Laboratory glassware (Pyrex™, Kimax™) has been found to contain trace metals. Fluoropolymer (PTFE, Teflon™) and plastic (linear polyethylene) labware are preferred as alternatives with the exception of colored plastics, which are known to contain metals. Plastic pipet tips may be a source of metals contamination and acid cleaned pipet tips are commercially available. Other materials that are known to contain trace levels of metals are rubber, paper cap liners, pigments in marking pens, polyvinyl chloride, nylon, methacrylate, Vycor™ and talc. It is necessary to use only clean, powder-free gloves for all sample handling steps.

Always test new products or similar products from a new manufacturer and do not make assumptions about the appropriateness of a product until it has been well tested. For low-level work, reagents should be ultrapure grade, or equivalent, and should never be returned to their stock containers once removed. Sample carry-over at the instrument must be carefully monitored and rinse times adjusted to eliminate any potential carry-over.

2.3 Cleaning Methods for Labware

All labware used during sample analysis must be free from metals contamination. Ideally, labware would be dedicated according to sample type and anticipated concentration of analytes. For example, sediments contain higher levels of metals than do tissues and the possibility of contamination will be minimized if labware for the different sample types are kept separate.

All labware should be thoroughly cleaned with a detergent solution (such as Detergent 8™), rinsed with metal-free water, and soaked overnight, or longer, in a covered acid bath containing a dilute nitric acid solution prepared from reagent grade nitric acid. A commonly used nitric acid bath concentration is 20 percent but other concentrations may be used if verified as adequate by the results of routine blanks. For example, some laboratories prepare labware for ultraclean work by soaking it overnight in hot concentrated nitric acid and find the use of hot acid particularly important for cleaning PTFE (Teflon™) labware. Other laboratories find that 5 percent nitric acid is sufficient for their work. Cleaning of labware for some analytes benefits from the additional step of a dilute hydrochloric acid soak.

Regardless of the strength or type of acid used, it is helpful if labware is stored containing dilute acid or in an acid bath until it is used, to prevent contamination during drying and storage. When labware is removed from the acid bath, it must be rinsed with copious quantities of metal-free water. The rinsing step is critical to minimize contamination. Acid baths should be changed periodically, as the acid becomes contaminated. To avoid contamination with chromium, do not use chromic acid for cleaning any materials.

The laboratory should have written procedures for labware cleaning methods. Verify the effectiveness of the labware cleaning methods and timing of acid bath changes by routinely analyzing blanks and maintaining documentation of blank results.

Acid precleaned plastic bottles and pipet tips are available commercially. Cleanliness of commercially cleaned labware should be monitored by the analysis of blanks.

2.4 Interferences

Marine samples provide a significant challenge to laboratories analyzing for trace metals. Sea water contains approximately 3 percent dissolved salts, which cause problems such as uneven sample transport rates and chemical and spectral interferences. Marine sediment digestates contain high concentrations of dissolved solids, from both interstitial sea water salts and salts resulting from sample digestion. Marine tissue digestates are also high in dissolved solids and dissolved organic material. The choice of analytical method must be made carefully and must account for potential interferences. The analyst should be experienced with analysis of marine samples and resolution of concomitant interference problems. Specific information on minimizing interferences from marine samples is found in sections of this chapter that cover the methods of analysis.

3. SAFETY CONSIDERATIONS

Each organization participating in a project should ensure that their activities do not increase the risk to humans or the environment. Laboratories must operate under an active safety program. Laboratory facilities need to have adequate ventilation for labware cleaning, sample preparation and instrumental analysis. Appropriate engineering controls and personal protective equipment must be available and used. Laboratory workers must be trained in safe laboratory techniques.

Health and safety issues need to be considered when choosing methods of analysis. When more than one method option exists, the method with fewer hazardous reagents, dangerous procedural steps or toxic by-products should be chosen. For cleaning of labware, care must be taken while using acid baths; acid fumes and potential for acid burns to skin and eyes can pose a risk. Temperatures and concentrations of acids should be kept as low as feasible for decontaminating labware and sampling equipment.

4. SAMPLE ACCEPTANCE AND STORAGE CRITERIA

All samples must be collected and handled following a sampling plan that addresses considerations discussed in Section 6, Sample Handling, of the Field Chapter (PSEP, 1997a). All sample containers should be prewashed according to the methods described in Section 2.5.2 of the Field Chapter. Alternatively, precleaned containers may be purchased.

When samples are received by the laboratory, adherence to the sample acceptance requirements specified in the project planning document should be verified to ensure sample integrity. The following should be considered:

- Technical validity - sample preservation and storage are appropriate for the stability of the analyte.
- Chain of custody - the personnel handling the sample are properly trained and authorized to do so; tampering with the sample is precluded and all sample handling is documented.

In addition, the following items should be verified: sample identification (between the sample container and the field sheet), sample bottles and sample receipt within holding time. When applicable, any safety hazards associated with the samples should be noted, documented and the appropriate personnel should be notified.

All samples should be preserved and stored according to applicable EPA approved procedures, as described in the Field Chapter (PSEP, 1997a), and analysis must start prior to expiration of holding time. Water samples for total metals analysis should be preserved with ultrapure nitric acid to pH < 2 at time of sampling. Marine and estuarine water samples have high ionic strength, resulting in a buffering capacity that impacts the amount of acid required for preservation. The pH of these samples should be confirmed and documented to be < 2 at time of preservation by pouring off a small amount of sample and checking it with short range pH paper. The pH should be checked again at the time an aliquot is removed for analysis. Excess acid should be avoided, however, as preconcentration techniques are strongly dependent upon pH. Suggested final concentration of nitric acid in the sample is 0.15 percent (EPA, 1992a) but pH must be checked carefully to ensure proper preservation of samples.

Often, samples are brought to the laboratory for preservation. If this is the case, samples should be kept cool ($4^{o}C$) during transportation and be preserved within 24 hours of sampling. When this is not practical, samples should be preserved as soon as possible and preserved samples must sit at least 16 hours prior to analysis to allow metals that may have plated onto the walls of the sample container to resolubilize.

Water samples for particulate or dissolved metals are filtered though 0.4 to 0.45 µm membrane filters prior to preservation. Filtering must occur as soon as possible after sampling and always within 24 hours. For this reason, field filtering is preferred but may not always be practical. When it is not feasible to filter samples for dissolved or particulate metals within 24 hours of collection, sample results may be qualified to reflect this. The filtrate, which contains the dissolved fraction, is preserved to pH < 2 with ultrapure nitric acid. The particulate fraction, which is retained on the filter, is preserved by freezing the filter. A convenient way to store filters frozen in a flat position is to transfer them to a clean, appropriately sized polystyrene Petri dish (PSEP, 1990). Metals samples are particularly prone to contamination during filtering and great care must be taken to minimize it. See Section 5.3.1 for further discussion of sample filtering.

Sediment and tissue samples should be kept cool during transport ($4^{o}C$) and tissue samples should be frozen at $-18^{o}C$ as soon as they arrive at the laboratory unless they are analyzed immediately. Sediment

samples for metals analysis may be stored at 4^{o}C for 6 months and 28 days for total mercury. However, Puget Sound Dredged Disposal Analysis (PSDDA) guidelines (U. S Army Corps of Engineers, 1991) specify that sediment samples requiring methyl mercury analysis should be stored frozen (-18^{o}C) and held for no more than 28 days. In the absence of supporting data, the storage of samples for total mercury at 4^{o}C for 28 days is acceptable. Recommended holding times for frozen sediment and tissue samples are 28 days for mercury and 2 years for other metals. Holding time for water samples is 28 days for mercury and 6 months for other metals.

If samples are to be frozen, sediment core samples should be divided into subsamples prior to freezing. Care must be taken to prevent container breakage during freezing. Head space should be left for interstitial water to expand, and containers should be stored at an angle rather than in an upright position.

Mercury is stable for at least one year in freeze dried sediment and tissue samples and this method has been adopted by the National Oceanic and Atmospheric Administration (NOAA) Status and Trends Program. In an unpublished study performed for Washington Department of Fish and Wildlife by the King County Metro Environmental Laboratory, fish muscle samples were analyzed for mercury before and after the 28 day holding time. Samples stored in glass and frozen at -18^{o}C were analyzed at 6 different times, ranging from 4 to 86 days after collection. No significant differences in the mercury concentrations were observed.

Tables 2, 3, and 4 of the Field Chapter (PSEP, 1997a) summarize appropriate sample containers, sample sizes, preservation techniques, storage conditions and holding times for trace metals analyses. Samples that are incorrectly preserved or not analyzed within holding times should be discussed in the narrative portion of the laboratory report and data may need to be qualified.

5. METHODS OF ANALYSIS

5.1 Method Selection

The selection of analytical methods for a project is influenced by a variety of factors. Some of these factors are client or program specifications, availability of accepted or standard methods, required detection limits, turn around time, sample type, available technology, operator expertise and economy. Additional analytical issues to consider include analytes to be measured, expected concentrations and potential interferences. The project manager and the analytical laboratory need to discuss project requirements during the planning stage so that the most appropriate analytical method is selected and documented in the project planning document. Appendix C to the QA Chapter (PSEP, 1997b) contains some program specific requirements for detection or regulatory limits.

This guidance document encourages the use of methods that produce comparable data so that data generated for a specific project can be used to support longer term environmental studies. In addition, project specific trend analyses require new data sets to compare with historical data sets. The use of EPA methods is recommended, when possible, for Puget Sound samples. Many laboratories routinely perform these methods and method performance is well documented.

When an appropriate EPA method is not available, a validated standard method from another recognized source, such as *Standard Methods for the Examination of Water and Wastewater* (APHA, 1992a), is recommended. When no standard method is available, the method chosen must be a written method and the laboratory must document method performance and ability to meet data quality objectives. The quality control section (9.0) of EPA analytical methods written in the Environmental Methods Management Council (EMMC) format (EPA, 1993 and EPA, 1994a) describes a detailed approach to assessing laboratory performance and data quality. In addition, it is recommended that highly complex methods only be used when essential for meeting project requirements. **The preferred approach is to use the most straight forward and standardized method available that meets data quality objectives.**

Methods for the determination of metals typically fall within the scope of a small number of instrumental methods and variations on those procedures. These include, but are not limited to, Flame Atomic Absorption (FLAA), Inductively Coupled Argon Plasma-Optical Emission Spectrometry (ICP-OES), Graphite Furnace Atomic Absorption (GFAA), Inductively Coupled Argon Plasma-Mass Spectrometry (ICP-MS), and Cold Vapor Atomic Absorption (CVAA) or Atomic Fluorescence (CVAF) for mercury.

Data provided by these different instrumental techniques are generally comparable where overlap of applicable concentration range occurs. Often, the choice of one over the other is based on expected concentration of the samples. In general, CVAA or CVAF techniques are usually the only options for mercury analyses, and ICP-OES is the most efficient method for many analytes when the detection limits are adequate to meet the needs of the client or program. Marine samples provide a significant challenge to laboratories analyzing for trace metals. Methods of analysis must be chosen that address specific interference problems and laboratories must develop experience with these methods and sample types.

5.2 Method Performance

5.2.1 Precision and Bias

Precision is an indication of the agreement among the results of replicate measurements. To estimate precision, the results for the replicate samples must be at or above the detection limit. If they are not, precision can be checked by analyzing replicates of check standards or matrix spikes. The best measure of precision is the relative standard deviation (RSD) or coefficient of variation (CV):

$$RSD=CV=100s_x/\bar{x}$$

where $\bar{x}$ is the arithmetic mean of the x_i measurements and s_x is the standard deviation.
The relative percent difference (RPD) is used when only two samples are available.

$$RPD = 100\frac{|x_1-x_2|}{(x_1 + x_2)/2}$$

The standard deviation can be calculated as follows:

$$S_x=\sqrt{\frac{1}{n-1}\left[\sum_{i=1}^{n}(x_i-\bar{x})^2\right]}$$

where n is the number of measurements.

Bias is described as the deviation due to a systematic error (i.e., a consistent tendency for results to be either greater or smaller than the true value), such as calibration error, matrix interference, inability to measure all forms of the analyte, analyte contamination, etc. Deviation due to matrix effects is assessed by comparing a measured value to an accepted reference value in a sample of known concentration (such as a standard reference material) or by determining recovery of a known amount of analyte spiked into a sample (matrix spike). Bias due to matrix effects based on a matrix spike is indicated by:

Bias = $(X_S - X_U) - K$,

where X_S is the measured value for the spiked sample, X_u is the measured value for the unspiked sample and K is the known (calculated) spike amount.

The percent recovery (%R) for check standard or matrix spikes is given by:

$$\%R=100(R_s/R_t)$$

where R_S is the result for the check standard or the difference between the results for the spiked and the unspiked samples and R_t is the known value for the check standard or the amount of the analyte added to the matrix spike.

Blanks can also be useful indicators of bias due to contamination. More information can be found in Section 6.6, Analytical QC.

Accuracy is described as the closeness of agreement between an observed value and a true or accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random (precision) component and of a systematic (bias) error component. Precision and bias are performance characteristics of the method used by a particular laboratory and analyst.

5.2.2 Determining, Defining and Verifying Detection Limits

Environmental analytical chemists have not universally agreed upon terminology for defining or conventions for determining and reporting lower detection limits for analytical procedure. The following guidance does not attempt to resolve the debate over terms or procedures for analytical detection limits. Rather, it is intended to provide practical information that can be used as a basis for discussion between program managers and laboratories.

EPA defines method detection limit (MDL) in Appendix B to 40 CFR Part 136 as "the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the element." A copy of the complete procedure is contained in Appendix E of the QA Chapter (PSEP, 1997b).

Actual detection limits may be affected by instrument sensitivity, bias due to contamination and/or matrix interferences. Common laboratory practice is to calculate MDLs to according the EPA procedure and subsequently adjust detection limits upward in cases where high instrument precision (i.e., low variability) results in calculated detection limits that are lower than the absolute sensitivity of the analytical instrument. In these cases, best professional judgment is used to adjust detection limits upward to a level where a signal can be routinely observed, recognizing that instrument optimization and performance does not remain constant under routine laboratory conditions. In addition, detection limits may be adjusted upward for some analytes when random contamination or interference is a significant issue for an analytical method.

The quantification limit represents a practical and routinely achievable level at which there is relatively good certainty that any reported value is reliable (APHA, 1992a). The quantification limit for a test is usually about five to ten times the detection limit and always higher than the detection limit. A quantification limit check standard should be analyzed to verify quantification limit at the instrument. A spiked method blank fortified with analytes at or near the quantification limit is also recommended as a periodic method check sample to demonstrate method performance near the quantification limit.

It is recommended that laboratories develop performance based control limits for low-level check standards. Further guidance on developing control limits can be found in the *EPA Handbook for Analytical Quality Control* (EPA, 1979) or Section 9.0 in the QC section of EPA methods written in the EMMC format (EPA, 1993). These control limits may be requested by project managers for inclusion into project planning documents. Certain projects may require verification of a laboratory's ability to meet regulatory action limits and this should be addressed in the project planning document.

Analyte values below the detection limit are not reported. Rather, the result is reported as less than the detection limit, including the numerical value for the detection limit. When an analyte value is between the detection limit and the quantification limit, the value is reported and is qualified as less than the quantification limit.

Some practical guidance for determining detection and quantification limits for inorganic analysis can be found in Appendix E.

5.3 Marine Water

Studies of metals in the water column may require analysis of the whole sample for total metals or separation of dissolved and particulate fractions, depending upon project objectives. Total metals are defined as the concentration of metals determined on an unfiltered sample after digestion. The dissolved fraction of a water sample is defined as the fraction that passes through a 0.4 or 0.45 µm membrane filter when an unpreserved water sample is filtered. The particulate fraction is defined as the material that is retained on a 0.4 or 0.45µm filter.

Pore size is important in this definition as particulate matter exists in the water column that is smaller than 0.45 µm. Several types of filters often used in the Puget Sound region have a nominal pore size of 0.4 µm. In practice, there is probably little difference in the material retained by filters with 0.45 and 0.4 µm pores sizes (PSEP, 1989). and subsequent discussion will refer to a 0.45 µm filter, but a 0.4 µm filter may be used as well.

5.3.1 Sample Preparation for Dissolved Metals

There is no detailed standard method available that addresses all the practical issues involved with the preparation of water samples for dissolved metals. The most critical concern when preparing samples for analysis of dissolved metals is contamination control. Utmost care and vigilance are required to filter samples without introducing metals contamination. Contamination during the sample collection, splitting and filtering steps is often a major source of bias. This results in false positive values for samples with low concentrations and limits the laboratory's ability to accurately measure metals at the low detection limits required for projects driven by water quality or human health criteria. Monitoring each step in the process with QC samples (blanks) is important to verify that analytical data represent sample concentrations and not sample contamination.

When filtering water samples for dissolved metals, two issues become important; finding a method and apparatus that minimizes contamination of the sample during the filtering process and has the ability to filter adequate volumes of sample in a reasonable amount of time. EPA Method 1669 (EPA, 1995b) describes a method for filtering samples for dissolved metals. The filter specified in the method is a tortuous-path capsule filter, such as the Gelman Supor™ 12175 or equivalent, used with either vacuum or pressure devices. While capsule filters are capable of filtering all types of water samples quickly without clogging, they are known to contribute contamination for some important elements, making them unsuitable for low-level trace metals work (Taylor and Shiller, 1995). In addition, tortuous-path capsule filters lack rigidly defined pore size which may result in additional filtering artifacts (Taylor and Shiller, 1995). For reasons of pore size consistency and contamination minimization, membrane filters are strongly recommended over capsule filters for marine water samples.

Membrane filters are available in several sizes, including 47 mm, 90 mm and 142 mm diameter sizes. The 47 mm diameter size is most commonly found in laboratories but larger filters may be necessary when filtering larger volumes of samples. EPA Method 1669 (EPA, 1995b), Section 6.17.2 describes the following method for acid cleaning 0.4 µm, 47 mm polycarbonate Nucleopore™ (or equivalent) membrane filters. Fill a 1 liter (L) fluoropolymer jar approximately two-thirds full with 1N nitric acid. Using fluoropolymer forceps, place individual filters in the fluoropolymer jar. Allow the filters to soak for 48 hours. Discard the acid, and rinse five times with metal-free water. Fill the jar with metal-free water, and soak the filters for 24 hours. Remove the filters when ready for use, using fluoropolymer forceps, and place them on the filter apparatus. Polycarbonate membrane filters often clog quickly. However, these filters have a lower potential for trace element contamination than alternatives such as

cellulose nitrate and cellulose acetate membrane filters.

Cellulose acetate or cellulose nitrate membrane filters do not clog as quickly as polycarbonate filters and can be mildly acid-cleaned using 10 percent HNO_3 (PSEP, 1990), although some laboratories have found difficulty in reducing contamination to acceptable levels with cellulose filters. Others recommend a second acid soak step using 20 percent HCl but cellulose acetate filters may disintegrate when subjected to HCl. It is important to test filters and filter cleaning processes thoroughly prior to use with real samples to verify control of metals contamination.

When using membrane filters, the filter-holding and sample capture equipment are also very important to the process. These must be made of an appropriate material, be acid-cleaned before use and rinsed well between samples. A Teflon™ in-line filter holder such as Millipore™ #XX434700 (or equivalent) works well and can be opened for filter change without disturbing the attached plumbing. Tubing that contacts the sample should be Teflon™. Fritted glass filter holders (use silicon stoppers) are easy to use during filtering but are difficult to clean well and do not filter samples as quickly as the in-line filter holders.

Other options in filtering equipment are available for dissolved metals. Any can be used so long as the final filter is 0.4 to 0.45 µm membrane and the samples are not contaminated by the filtering process. Filtering may need to occur in a clean room if necessary to meet required detection limits. If using a pressure filter device, filter at a pressure of 70 to 130 kPa. Pressure filter units clog less readily than vacuum filters (APHA, 1992b).

A method follows for filtering samples in the laboratory for dissolved and particulate metals analysis. This method is offered as an example and may be modified depending upon filter apparatus. Only unacidified samples should be filtered. The volume to filter depends upon the tests being run on each sample (it is important to remember that mercury is a separate test and that additional sample is required for duplicates and matrix spikes). If collecting the particulate fraction, the sample must be shaken thoroughly immediately before subsampling to achieve a representative sample. If collecting only the dissolved fraction, allow particulates to settle or centrifuge the sample to minimize filter clogging. If total and dissolved metals samples are to be taken from the same container, take a subsample for total metals before allowing particulates to settle.

1. Conduct filtering in a clean room or on a clean bench **when needed to meet required detection limits**. Set up acid-cleaned filtering apparatus, with filter in place. Use Teflon™-coated forceps for handling filters.

2. Rinse the system by filtering at least 1L of metal-free water and discarding the rinse water.

3. Collect a "before" filtrate blank by filtering 500 milliliters (mL) of metal-free water through the system. Collect the filtrate, transfer it to a 500 mL acid-cleaned sample bottle and label the bottle with date and associated sample batch.

4. Rinse the filtering apparatus with sample by filtering a portion of the sample and discarding this portion. Filter required volume of sample and retain the filtrate for dissolved metals analysis. If the filter clogs, change filters. Centrifuging the sample or prefiltering with a 3 µm or 1 µm filter may also minimize filter clogging. Be aware that additional steps or filters used in the filtering process increase potential for sample contamination. Centrifuging, prefiltering and changing filters when clogging occurs are not options when collecting particulate metals samples. See 5.3.2, below for more information about particulate metals.

5. Thoroughly rinse filtering apparatus with at least 1L of metal-free water between samples. Repeat steps 4 and 5 for additional samples. Decontaminating the apparatus between samples by rinsing with dilute (1 percent) nitric acid may be necessary, depending upon sample concentrations and required detection limits.

6. At the end of the sample batch and after decontaminating filtration apparatus, collect an "after" filtrate blank as in step 3.

7. Preserve the filtered samples and blanks with ultrapure nitric acid to pH < 2. Dissolved metals samples are now ready for analysis. Place filters for particulate metals analysis in pre-cleaned polystyrene Petri dish for freezing or to a digestion vessel for analysis.

Generally, filtered, fresh water samples for dissolved metals do not require any additional sample preparation prior to instrumental analysis, unless a precipitate forms on acidification. If this occurs, digestion of the acidified filtrate is required. For marine water samples, however, additional sample preparation may be required to minimize the effects of the sea water matrix. Refer to Section 5.3.4.1 below for more information on matrix removal techniques.

5.3.2 Sample Preparation for Particulate Metals

Particulate metals are defined as metals retained by a 0.45 µm membrane filter when an unpreserved water sample is filtered. Theoretically, the arithmetic difference between total and dissolved metals results would yield data for the particulate metals fraction. This approach may be appropriate for the objectives of some projects while others may require direct analysis of the particulate fraction. This decision can be influenced by the expected levels of analytes in the dissolved fraction, as it is difficult to take the difference between total metals and dissolved metals when either or both contain analytes at concentrations below the detection limit. For the direct determination of particulate metals, the material retained on the filter is digested and analyzed. When preparing a sample for particulate metals analysis, it is important to collect enough sample on the filter to achieve the detection limits required by the project. The weight of particulate and the volume of water filtered must be recorded if metals concentrations are to be reported on a weight basis. If metals concentrations are to be reported on a volume basis, only the volume of sample filtered needs to be recorded. The expression of particulate metals results on a weight or volume basis must be specified in the project planning document.

When particulate metals results are to be expressed on a weight basis, there are several considerations for obtaining all the relevant data. Filters may clog quickly, making it difficult to filter enough sample so that particulate is collected in sufficient quantities to both be weighed accurately and to result in detectable levels of metals in the digested sample. In addition, metals contamination can occur during the filter drying and weighing process, biasing the results.

One approach is to perform a 0.45 µm suspended solids test concurrently with collection of the particulate metals sample. The volume of water filtered for both the metals test and the suspended solids test is recorded so the metals results can be converted to a weight basis using the suspended solids results. With this approach, the filter holding the particulate metals sample would not undergo the additional drying and weighing steps that may contribute contamination. Even so, it is difficult to collect enough particulate material to weigh accurately before the filter clogs.

Depending on the amount of particulate matter in the sample, the approximate volume of sample recommended for filtering for particulate metals is 4L. If it is impractical to collect enough volume of water for both a particulate metals sample and a 0.45 µm suspended solids test, a drying temperature of 60^{o}C is recommended to minimize the loss of more volatile elements. The 142 mm diameter filters may

be required to filter the recommended 4 L sample volume. See Section 4.2.2 of the Field Chapter for additional guidance on field filtering for dissolved and particulate metals.

Particulate metals samples require digestion prior to analysis. Since a standard method is not available for digesting particulate metals samples, it is recommended that the sediment digestion method (EPA Method 3050 (EPA, 1992b) discussed in Section 5.4.1.2 be used and that the acid amounts be modified according to particulate weight and final digestate volume. Final digestate volume can be minimized to reduce the detection limit.

A sensitive determinative method, such as GFAA or ICP-MS may be required to quantitate analytes in the digestates. It is important to matrix match the final concentration of the acids in the digestate with the instrument calibration standards. Include a clean filter in the method blanks to determine the presence or absence of metals contamination from the filters. Analyzing several blanks, is recommended. Results are reported on a weight basis, using 0.45 µm suspended solids results to make the conversion. Additional guidance on particulate metals can be found in the PSP&G Freshwater Metals Chapter (PSEP, 1990).

5.3.3 Sample Preparation for Total Metals

Total metals are defined as the concentration of metals determined on an unfiltered sample after digestion. Unfortunately, there are only a limited number of EPA methods available at this time for trace metals analyses of marine waters. In addition, there is no standard approach to sea water testing currently among the Puget Sound region trace metals laboratories. While some sea water samples may contain analytes at or above nominal instrument detection limits, the complexity of marine matrices will often limit the capability of the instrument to achieve routine detection limits. Ambient concentrations of many metals in sea water are so low and the sample matrix so challenging, that routine analytical methods are often not adequate to satisfy program needs.

Sea water contains approximately 3 percent dissolved salts and pretreatment of samples is often required. The appropriate pretreatment method must separate the matrix from the analytes while maintaining or lowering detection limits. Some of the more sensitive instruments, such as newer ICP-MS models, may be capable of analyzing samples of marine water directly, after dilution at a ratio of approximately 1/100. When such instruments are available, a simple technique such as dilution is preferred to complex sample preparation techniques.

When high sensitivity instruments are not available, or when detection limit requirements for marine water samples are very low, other pretreatment techniques may be necessary. Pretreatment techniques such as on-line and off-line chelation preconcentration, chelation/solvent extraction, coprecipitation and reductive precipitation all perform some preconcentration of trace elements while modifying the sample matrix sufficiently for effective instrumental analysis.

A good deal of attention is currently being devoted to the field of pretreatment techniques that combine matrix modification with preconcentration. These procedures are intensive in terms of time, labor, analyst expertise and cleanliness and typically combine the matrix modification/preconcentration step with the standard determinative methods available in most analytical laboratories. While matrix removal methods usually cite a specific determinative method, this may be flexible, and matrix removal methods may be compatible with other determinative methods. Furthermore, on- and off-line techniques may be interchangeable with appropriate modifications.

While some sample matrix removal/preconcentration methods have been published by the EPA, the scope of these procedures is currently less than comprehensive. Other research level methodologies are

available through industrial and academic sources. In the absence of standard methods, the use of non-standardized methods and/or performance based methodology may be necessary to meet project requirements. The currently available validated EPA methods for matrix removal and preconcentration are described in Section 5.3.4.1 below. Validated EPA methods for direct analysis of sea water are described in Section 5.3.4.2, mercury methods are described in Section 5.3.4.3 and a draft EPA method for the hydride generation technique for arsenic analysis is described in Section 5.3.4.4. Research level methodologies for matrix removal/preconcentration are described and referenced in Appendix D.

Table 2 (EPA, 1994b) provides a summary of the EPA Marine Ambient Water Quality Criteria for metals. Table 3 shows examples of ambient levels of metals in sea water. These tables are intended to provide comparative information about sea water trace metals concentrations and potential project goals in support of Puget Sound programs.

Table 2
EPA Ambient Water Quality Criteria for Total Recoverable and Total Dissolved Priority Pollutant Metals (EPA, 1994b)

	Ambient Water Quality Criteria[1] (µg/L)					
	Marine Criteria				Human Health Criteria	
Element	Acute[2] Total Recoverable	Acute[3] Total Dissolved	Chronic[2] Total Recoverable	Chronic[3] Total Dissolved	H_2O/Organism[2] Total Recoverable	Organism[3] Total Recoverable
Antimony	--	--	--	--	14[4]	4300[4]
Arsenic	69	65.6	36	34.2	0.018[4]	0.14[4]
Cadmium	43	36.6	9.3	7.9	--	--
Chromium (VI)	1100	1050	50	47.5	--	--
Copper	2.9	2.5	2.9	2.5	--	--
Lead	220	110	8.5	2.1	--	--
Mercury	2.1	1.8	0.025	--[5]	0.14	0.15
Nickel	75	64	8.3	7.1	610[4]	4600[4]
Selenium	300	--[5]	71	--[5]	--	--
Silver	2.3	2.0	--	--	--	--
Thallium	--	--	--	--	1.7[4]	6.3[4]
Zinc	95	81	86	73	--	--

(1) WQC promulgated in the National Toxics Rule (NTR) for 14 states at 40 *CFR* Part 131 (57 FR 60848). Criteria for metals listed at 40 *CFR* Part 131 are expressed as total Recoverable at a hardness of 100 mg/L $CaCO_3$ and a water effect ratio (WER) 1.0.

(2) As listed in the NTR at 40 *CFR* Part 131 for total recoverable metals.

(3) For cadmium, copper, nickel, and zinc, acute and chronic criteria for dissolved metals and metal species were calculated by taking 85 percent of the corresponding total recoverable criteria level. For arsenic and chromium(VI), acute and chronic criteria for dissolved metals and metal species were calculated by taking 95 percent of the corresponding total recoverable criteria levels. For lead, acute dissolved criteria were calculated by taking 50 percent of the corresponding total recoverable level; for lead chronic criteria, dissolved criteria were calculated by taking 25 percent of the total recoverable levels. Dissolved values for mercury chronic criteria and selenium acute and chronic criteria were not calculated because these metals bioaccumulate, and dissolved criteria would not be appropriate. (*Guidance Document on Dissolved Criteria: Expression of Aquatic Life Criteria,* October 1993. Attachment 2 to memorandum from Martha Prothro to Water Mgmt. Division Directors, October 1, 1993.)

(4) Criterion reflects recalculated value using IRIS.

(5) Metal is bioaccumulative and, therefore, it is not appropriate to calculate WQC for dissolved levels. (*Guidance Document on Dissolved Criteria: Expression of Aquatic Life Criteria,* October 1993. Attachment 2 to memorandum from Martha Prothro to Water Management Division Directors, October 1, 1993.)

Table 3

Ambient Concentrations for Trace Metals in Puget Sound

	Trace Metal Concentrations (µg/L)							
	Arsenic	Cadmium	Copper	Mercury	Nickel	Lead	Silver	Zinc
Inner Elliott Bay[1]	--	0.097	0.94	--	0.50	0.55	--	2.2
Outer Elliott Bay[1]	--	0.073	0.63	--	0.47	0.37	--	0.83
Puget Sound, Main Basin[1]	--	0.104	0.47	--	0.41	0.08	--	0.60
Admiralty Inlet[1]	--	0.085	0.19	--	0.31	0.025	--	0.29
Puget Sound, unspecified location[2]	1.5	0.05	0.25	0.001	0.25	0.05	0.002	0.5
Open Ocean Seawater[3]	1.26	0.016	0.228	--	0.228	0.013	--	0.115

Notes:
[1] Paulson et al. (1985).
[2] PSEP, 1989.
[3] National Research Council of Canada (NRCC) NASS-4 certificate values - see Appendix A for source.

5.3.4 Methods of Analysis for Marine Water Samples

5.3.4.1 Methods with chelation matrix removal and preconcentration steps

EPA Method 200.10 *Determination of Trace Elements in Marine Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma - Mass Spectrometry* (EPA, 1992a).
EPA Method 200.13 *Determination of Trace Elements in Marine Waters by Off-Line Chelation Preconcentration with Graphite Furnace Atomic Absorption* (EPA, 1992c).

These methods are used to preconcentrate trace elements using an iminodiacetate functionalized chelating resin. Acid solubilization (digestion) is required prior to chelation to break down complexes of colloids that might influence trace element recoveries. Chelation procedures offer the ability to concentrate analytes of interest while at the same time removing undesirable sample constituents from the sample matrix. Pre-assembled iminodiacetate units are commercially available. One drawback of this approach is that no single chelation chemistry has been found to be applicable to all of the analytes commonly of interest. EPA 200.10 is applicable to cadmium, cobalt, copper, lead, nickel, uranium, and vanadium. The detection limits given in EPA Method 200.10 (EPA, 1992a) were determined with reagent water. The detection limits reported in the method are lower than EPA Marine Water Quality Criteria. EPA 200.13 is applicable to cadmium, cobalt, copper, lead, and nickel. Detection limits for EPA Method 200.13 (EPA, 1992c) were determined for cadmium, copper, and lead using the NRCC reference material NASS-3. These detection limits are lower than the EPA Marine Water Quality Criteria. No detection limits are listed in the method for cobalt and nickel.

5.3.4.2 Methods without matrix removal and preconcentration steps

5.3.4.2.1 ICP-OES

EPA Method 200.7 *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry* (EPA, 1994c).

EPA Method 200.7 (EPA, 1994c) could be used for analysis of some elements in sea water by ICP-OES after appropriate digestion for total metals and filtration for dissolved metals. However, ICP-OES is not an adequately sensitive technique for measuring trace elements in sea water. ICP-OES could be used to analyze for major elements such as calcium, magnesium, potassium, and sodium in sea water and samples may require considerable dilution to bring some analytes within linear range of the instrument. Samples and standards should be matrix matched, and a serial dilution analysis should be performed to verify that physical and chemical interferences are not present. Analyzing samples that are high in dissolved solids causes salt to build up on the plasma torch, and frequent instrument maintenance is required to prevent problems such as carry-over.

5.3.4.2.2 GFAA

EPA Method 200.12 *Determination of Trace Elements in Marine Waters by Stabilized Temperature Graphite Furnace Atomic Absorption* (EPA, 1992d)

EPA Method 200.12 (EPA, 1992d) describes a method for analyzing sea water directly by GFAA after digestion for total recoverable analytes or filtration for dissolved analytes. The method applies to some but not all of the elements that are listed in the EPA Marine Water Quality Standards. The elements addressed by the method include arsenic, cadmium, chromium, copper, lead, nickel, and selenium. Detection limits listed in the method were determined in a sea water matrix and are lower than the EPA Marine Water Quality Standards for most elements, but higher than ambient levels of trace elements in marine waters. Instruments equipped with Zeeman background correction, delayed atomization furnace and capability to alternate gas supply are specified in this method.

5.3.4.2.3 ICP-MS

EPA Method 200.8 *Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma- Mass Spectrometry* (EPA, 1994d).

EPA Method 200.8 (EPA, 1994d) describes a method for analyzing total and dissolved metals by ICP-MS. ICP-MS is relatively new technology for routine environmental analyses and is more complex than previously existing metals analytical techniques. This technique is well suited to clean samples with low dissolved solids. EPA Method 200.8 (EPA, 1994d) recommends that dissolved solids not exceed 0.2 percent (weight/volume). However, low detection limit capabilities, large linear dynamic range and ability to analyze for several elements simultaneously also make it an attractive technique for more challenging matrices, including marine samples.

Sea water samples can be analyzed directly for some elements by ICP-MS if samples are diluted significantly. However, sample dilution increases detection limits by the same amount. In addition, ICP-MS is subject to both physical and chemical interferences. High dissolved solids present in sea water affect sample nebulization, transport and ion transmission efficiency. Analyzing samples with high dissolved solids content can lead to deposition of solids on the nebulizer and on the sampling and skimmer cones of the ICP-MS, requiring short runs and frequent cleaning. High levels of chloride are present in marine waters, causing isobaric interferences on arsenic (ArCl), chromium (ClOH), nickel (NaCl) and selenium (ArCl, ScCl).

Because of the complex nature of this technique and the potential for high productivity, the following guidance on potential interferences is offered for the application of ICP-MS to marine samples. The use of matrix removal techniques minimizes these potential interferences.

5.3.4.2.3.1 Interferences on ICP-MS

Certain circumstances, such as interferences ($ArNa^+$ on $^{63}Cu^+$) or instrument drift caused by analyzing samples with high dissolved solids, may necessitate the use of alternate isotopes for analytical determinations. Initial demonstration of performance (EPA, 1994h) for all potential isotopes that fall

into this category should be verified. Detection limits and linear ranges should be clearly documented for all isotopes that may be used. Corrections for chloride isobaric interferences must be applied regardless of the digestion techniques used, due to the high levels of chloride that are certain to be present in marine samples. This pertains especially to vanadium (ClO) and arsenic (ArCl) for which interelement corrections are already prescribed in the method.

It is important to note that the correction equations listed in the method are limited to chloride concentrations up to 0.4 percent. In addition, the presence of bromine in sea water results in a false positive error caused by the correction equation for selenium (BrH) on arsenic. Both ^{82}Se and ^{77}Se should be monitored and compared. Increased values for ^{82}Se may indicate an interference on arsenic due to bromine and alternate method of analysis such as hydride generation or GFAA may be required. Other analytes that may be affected are chromium (ClOH), nickel (NaCl), and selenium (ArCl, ScCl). ^{63}Cu should be monitored because of potential interference on ^{63}Cu from sodium (ArNa). ^{60}Ni is subject to interferences from calcium, magnesium, sodium, and chloride. The analyst should be conscious of these possibilities when experiencing difficulties and when assessing data quality.

Most interelement correction factors in use today are based on isotope ratios (relative abundances) of the elements involved in the measurement. Isotope ratios are fixed for most elements, but instrumental bias will affect the apparent, or measured, isotope ratio. The accuracy of the correction depends on the accuracy of the measured isotope ratios and instrumental factors such as drift and optical tuning.

A serial dilution of one sample per matrix in each batch would serve as an indication of matrix effects. Difference in recoveries outside the range of ± 10 percent indicate a matrix interference. Serial dilution of a matrix spike could be more comprehensive because all analytes of interest are certain to be present at adequate concentrations for a meaningful test.

5.3.4.3 Mercury Methods

EPA Method 245.1 *Determination of Mercury in Water by Cold Vapor Atomic Spectrometry* (EPA, 1994e).

EPA Method 245.7 *Determination of Mercury by Automated Cold Vapor Atomic Fluorescence Spectrometry* (EPA, 1994f).

Mercury can be analyzed for according to EPA Method 245.1 or 245.7, (EPA, 1994e and EPA, 1994f) depending upon the detection limit requirements of the project and the concentration of mercury in the samples. The range of application for EPA 245.1 (EPA, 1994e) is 0.2 µg/L to 20 µg/L and the range of application for EPA 245.7 (EPA, 1994f) is 0.002 µg/L to 25 µg/L. Both methods are applicable to sea water. The detection limit of the atomic fluorescence method can be reduced to 0.2 ng/L if a preconcentration (gold amalgamation) step is added to the method. EPA Method 1631 (EPA, 1995c, Draft) describes the gold amalgamation apparatus and procedure and provides information for sample collection, shipping and analysis to prevent contamination at these very low concentrations of mercury.

5.3.4.4 Hydride Generation

EPA Method 1632*: Determination of Inorganic Arsenic in Water by Hydride Generation Flame Atomic Absorption,* (EPA, 1995d, **Draft**).

EPA Method 1632 (EPA, 1995d, Draft) for analysis of arsenic in water hydride generation is, at this point in time, a draft method. This method does not apply specifically to sea water and no performance criteria are mentioned in the method for sea water matrices.

Inorganic and organic arsenic is converted to volatile arsines using 6 molar hydrochloric acid and 4 percent sodium borohydride. Arsines are purged from the sample onto a cooled glass trap packed with 15 percent OV-3 on Chromasorb® WAW-DMCS. The arsines are then thermally desorbed, in order of increasing boiling points, into an inert gas stream that carries them into the flame of an atomic absorption spectrophotometer for detection. The first to be desorbed is AsH_3, which represents total inorganic arsenic in the sample and the detection limit is 0.01000 µg/L.

5.4 Marine Sediment

5.4.1 Sample Preparation

It is extremely important that a precise definition of what constitutes the sample to be analyzed is contained in the project planning document. References for organics analyses recommend that excess overlaying water in a sample be decanted prior to subsampling (PSEP, 1997c). This is not recommended for metals analysis, however and overlaying water must be stirred into the sample. Samples may then be analyzed wet, may be dried at room temperature, may be oven dried at 60^{o}C or freeze-dried. Analysis of wet or freeze-dried samples is preferred when it is important to retain the particle size distribution of the original sample (ASTM, 1995a). Care should be taken in the drying process to minimize volatilization of analytes and contamination of the samples.

Metals results are usually reported on a dry weight basis and a separate aliquot is taken for solids determination and dried at 105^{o}C. It is important to use the correct conversion of metals results to dry weight basis if samples are dried before metals analysis at a temperature other than 105^{o}C (ASTM, 1995b). In addition, it is important that sediment samples are handled consistently by all laboratory departments to avoid inconsistencies in converting metals results to a dry weight basis. A separate aliquot for percent solids may be taken for each sample pretreatment procedure and dry weight values calculated using the appropriate percent solids value. A large error in dry weight values will be realized if aliquots with varying amounts of water are obtained for each chemistry test and the percent solids (moisture) determination.

When taking an aliquot for metals or solids analysis, mix the sample well in sample container with a spatula to homogenize. It can be difficult to obtain a representative aliquot with samples that contain a large proportion of interstitial water and it is important that the analyst make every attempt to obtain a representative aliquot. In some cases, withdrawing the sample with a 5 mL plastic pipet with the tip cut off is an effective method of obtaining an aliquot of samples of this nature.

Preparation of elutriates should follow the procedures in *Evaluation of Dredged Material for Discharge in Waters of the U.S. - Testing Manual-Draft* (EPA, 1994g).

5.4.1.1 Sample digestion and analysis for total mercury

EPA Methods 7471 and 245.5 (EPA, 1994h; EPA, 1991a) are applicable to sediments. These methods use aqua regia as part of the digestion process and result in good recoveries for total mercury in marine sediments. The use of aqua regia rather than the nitric/sulfuric acid mix specified in EPA Method 245.1 (EPA, 1994e) is particularly important for samples that are highly organic in nature. In an unpublished study performed at the King County Environmental Laboratory, low mercury recoveries were observed for such samples when aqua regia was not used.

5.4.1.2 Sample digestion for all elements except mercury

Most marine sediment metals analyses conducted in support of the major Puget Sound programs to date have been prepared by one of two digestion methods:

- Total dissolution using hydrofluoric and other strong acids.
- Strong acid digestion using nitric and hydrochloric acids and hydrogen peroxide.

Total dissolution, also known as Total Acid Digestion (TAD) completely dissolves the silicate minerals, so that recoveries are complete. Strong Acid Digestion (SAD) dissolves nearly all the heavy metals in fine-grained sediments, including cadmium, copper, lead, mercury, silver, and zinc, but does not dissolve all the minerals. Elements that are not recovered completely by the strong acid digestion include iron, aluminum, manganese, chromium, and nickel. Chromium is listed under the Sediment Management Standards (SMS) (Appendix C, PSEP, 1997b) and nickel is monitored by the PSDDA Program (Appendix C, PSEP, 1997b).

The recommended digestion method for sediments is the strong acid digestion, EPA Method 3050 (EPA, 1992b), rather than the total acid digestion. The majority of the analytical laboratories that routinely support Puget Sound programs use the strong acid digestion preferentially over the total acid digestion method for technical, safety, waste stream and cost reasons. Several of these laboratories reported difficulties in routinely analyzing samples using the total acid digestion. Total acid digestates contain high dissolved solids that cause physical and spectral interferences for all the determinative methods. The interferences can be severe enough to require dilution of the digestate, resulting in higher detection limits. The strong acid digestate does not contain such high dissolved solids and can be analyzed directly by FLAA, GFAA, ICP-OES, or ICP-MS. In addition, laboratory managers have expressed concerns over the serious safety and laboratory waste stream issues associated with the use of hydrofluoric and perchloric acids and questioned whether the trade-offs for data use outweighed the worker health and safety concerns and increased analytical costs.

5.4.2 Instrumental Analysis

Detection limit requirements for sediments collected for the major Puget Sound programs are listed in Appendix C of the QA Chapter (PSEP, 1997b). A general recommendation is to use an analytical method that is capable of achieving a detection limit that is 3 times lower than the project specific detection limit requirements. Although this is not always possible, and is not required by the programs, the usefulness of data near the regulatory limits is enhanced if the data are not subject to the analytical variability inherent near the detection limit. All of the instruments described below are approved by EPA for analysis of sediment digestates and will produce comparable data if care is taken by the analyst to reduce the effects of matrix interferences. The choice of instrumental method is determined by sample concentrations and the required detection limit. Cold Vapor Atomic Absorption or Cold Vapor Atomic Fluorescence are the recommended techniques for analysis of mercury in marine sediments. A separate sample aliquot is prepared for mercury analysis by EPA method 7471 (EPA, 1994h).

Simultaneous ICP-OES is often used for marine sediment work because several elements can be analyzed for at the same time and detection limit capabilities are sufficient for most Puget Sound programs. ICP-OES analyses can be subject to interelement interferences. The analyst must be aware of the potential for interferences and set up interelement correction (IEC) factors for these. The EPA reference methods include tables of potential interfering elements and their effects on specific analytes. In addition, the reference methods include recommendations for interference check solutions that are analyzed during each sample run to verify interelement and background correction factors. It is the responsibility of the analyst to become familiar with the potential interferences for marine sediment samples and to correct for them. The use of wavelength scans can be helpful in determining the effect of spectral interferences on ICP-OES results and to identify potential interferences for which there are no analytical channels on the particular instrument in use.

5.5 Marine Tissue

5.5.1 Sample Preparation

Tissue sample resection and subsampling is conducted by a knowledgeable biologist prior to delivery of samples to the analytical laboratory. Information on resection can be found in the Field Chapter (PSEP, 1997a).

5.5.1.1 Homogenization

Tissue samples must be homogenized prior to digestion to ensure that aliquots for analysis are representative of the organism and to improve digestion efficiency. Minimize sample handling during this step to reduce the risk of contamination. If samples are to be analyzed for other parameters in addition to metals, consider the contamination issues for sample handling of all parameters during the homogenization step.

Thaw frozen samples immediately before homogenizing. Larger samples may be cut into 2.5 cm cubes with titanium, quartz or high quality stainless steel knives before grinding or homogenizing. Tissue grinders or homogenizers are commercially available. For metals analysis, choose a grinder with blades made of titanium, tantalum or high quality stainless steel. Stainless steel should not be used, however, if chromium and nickel are analytes of interest. If chromium and nickel contamination are not of concern, a

Waring type blender with stainless steel blades and an acid-washed glass jar can be used. A rinsate blank should be collected from the homogenization apparatus to verify that decontamination procedures are sufficient.

When homogenizing the samples, include any liquid that is present with the sample. When possible, homogenize the sample in the sampling container. The sample should be homogenized to a paste-like consistency. No chunks should remain in the sample because these may not be extracted or digested efficiently. Homogenized samples must be stored frozen, thawing only for analysis.

There are times when the amount of sample available may be severely limited, such as with organ tissue. If this is the case, it is particularly important to conserve sample during the homogenization step. Choose a grinder that is designed for small sample sizes and homogenize the sample in the original sample container to avoid loss in the process of transferring sample from one container to another. In addition, it may be necessary for the project manager to assign priority of analyses when sample size is limited.

Samples may also be freeze-dried and homogenized by pulverizing prior to analysis. Freeze-drying may result in a more representative sample for large whole body fish and mollusks when homogenizing wet is not practical. In addition, freeze-drying prior to digestion may facilitate a more complete digestion of fatty tissues. A disadvantage of freeze-drying is the additional step, which increases the potential for sample contamination. Certified reference tissues are generally freeze-dried to facilitate long term storage of the materials as most biological processes are suspended by freeze-drying.

5.5.1.2 Digestion

Most marine tissues analyzed in support of the major Puget Sound programs have been digested by one of the following methods:

- nitric acid/perchloric acid or
- nitric acid/hydrogen peroxide.

For each of these, there are several options for the methods of sample heating, including open vessel/hot plate, digestion bomb/oven and closed vessel/microwave digester. The above digestion methods produce similar results, with the nitric acid/perchloric acid digestion producing potentially better recoveries on tissues high in fat content. However, there are several disadvantages to the nitric acid/perchloric acid digestion, including safety concerns associated with the explosive nature of perchloric acid and the need for a specialized perchloric acid fume hood. In addition, perchloric acid digestates are more difficult to analyze than peroxide digestates for low levels of metals, because of interference problems for both GFAA and ICP-MS. For these reasons, hydrogen peroxide is the recommended approach.

EPA Method 200.3 (EPA, 1991b), describes a method for the nitric acid/hydrogen peroxide hot plate digestion. This particular method includes a hydrochloric acid step at the end of the digestion. This step is recommended for improving recovery of antimony and silver but could result in chloride interferences for some elements on GFAA and ICP-MS and is not recommended for analysis of elements other than antimony and silver.

5.5.2 Instrumental Analysis

Detection limit requirements for the Puget Sound Ambient Monitoring Program (PSAMP) Fish Task are found in Appendix C of the QA Chapter (PSEP, 1997b). In general, programs such as this are focused on monitoring elevated levels of metals in fish tissue to support public health studies. In addition, these programs monitor long term trends at both clean and contaminated sites. Therefore, more sensitive instrumental methods are often required to meet program needs. The following instrumental methods are suitable for analysis of tissue samples, depending upon sample concentrations and required detection limits.

ICP-OES and FLAA can be used for elements such as copper and zinc that are present in the samples at quantifiable levels for these instruments. ICP-MS or GFAA are required for elements such as lead that are found in very low concentrations. CVAA is the recommended technique for analysis of mercury in marine tissues unless detection limit requirements are very low and samples are not contaminated. When lower detection limits are required, CVAF is recommended. A separate sample aliquot is prepared for mercury analysis using EPA Method 245.6 (EPA, 1991c), which includes both sample preparation and instrumental analysis methods.

Tissue samples are challenging to analyze due to the presence of fat, high dissolved solids and other interferences. Instrumental analysis of tissue digestates requires experimentation with instrument conditions to minimize the effects of interferences. The analysis of sufficient QC checks is required to verify that interferences have been overcome (e.g. GFAA analytical spikes). Increased frequency of routine instrument cleaning and maintenance is also necessary to prevent analytical problems resulting from dirty instrument components.

5.6 Analytical Quality Control

All EPA methods include specific recommendations for QC samples, control limits and corrective actions. The approach to analytical QC varies somewhat among the different EPA methods depending upon the data usage that the method was intended to support. In choosing an approach to analytical QC, a laboratory should keep in mind that QC sample results help define both method performance and data quality. The appropriate level of QC for a given set of samples is impacted by the complexity of the analytical method, the sample matrix and the project required detection limits. In addition, the level of QC, control limits and corrective actions are impacted by the end use of the data.

Analytical QC for each project must be specified in the project planning document and reflect an agreement between the project manager and the laboratory before the analysis begins. This is particularly important when project specific QC is more stringent than the method QC. In addition, the QC required for a project must take into account any subsequent program driven data qualification. Appendix C to the QA Chapter (PSEP, 1997b) summarizes many of the program specific requirements for QC.

EPA methods that follow the EPA Environmental Methods Management Council's (EMMC) *Format for Method Documentation* (EPA, 1993*)* are performance based and include comprehensive QC procedures and acceptance criteria in Section 9.0. These QC procedures provide useful guidance for implementation of new methods. In addition, Section 9.0 describes a method for determining control limits for QC

samples from internal laboratory performance data.

All quality control documentation should be maintained and available for easy reference or inspection. Following is a summary of minimum required QC samples and control limits for trace metals analysis. This section is not intended to provide criteria that are more lenient than the reference methods. Rather it provides guidance when reference methods do not include specific QC procedures, as in the case of the experimental methods found in Appendix D of this chapter. In addition, this section provides guidance for preparing project planning documents.

5.6.1 Instrument Quality Control

5.6.1.1 Calibration

Although calibration is not considered a QC procedure, it is included in this section for continuity. The procedure used for calibration of analytical instruments directly affects the accuracy of analytical results. For trace metals work, it is important to compare daily instrument readings for calibration standards with typical readings for an optimized instrument. If readings for the standards are inconsistent with expected readings, the instrument may need to be optimized and recalibrated. For example, calibration blanks contaminated with analytes could cause a negative bias in the data This would impact the accuracy of the data, particularly near the detection limit.

Analytical instruments must be calibrated daily or each time the instrument is run, with a calibration blank and at least three calibration standards for most instruments. A blank and one calibration standard is acceptable for ICP-OES. Standards should be matrix matched to the samples, matching acid composition and strength of standards and samples (EPA, 1992e) and, in the case of sea water samples, standards may need to be prepared with synthetic sea water. A recipe for synthetic sea water can be found in ASTM, Section 11.02, D1141-90 (ASTM, 1995c).

5.6.1.2 Initial calibration verification (ICV)

Run immediately after calibration, the ICV is an instrument check sample containing all analytes of interest at a concentration above the quantification limit. The ICV must be prepared from a different source (different bottle of stock solution) than calibration standards. Calculated concentration values should not deviate from the actual values by more than 10 percent for ICP-OES, GFAA and ICP-MS and 20 percent for mercury (or performance based intralaboratory control limits, whichever is lower). If values for the ICV are outside the control limits, the instrument run is stopped, the problem is corrected, the instrument is recalibrated and calibration is verified with another ICV.

5.6.1.3 Initial calibration blank (ICB)

Immediately after calibration verification, analyze a calibration blank. If the absolute value of the blank exceeds the detection limit, the analysis should be terminated, the problem corrected, the instrument recalibrated as necessary and the calibration reverified.

5.6.1.4 Continuing calibration verification (CCV)

Every 10 samples, analyze a CCV check sample containing all analytes of interest at a concentration above the quantification limit. Calculated concentration values obtained should not deviate from the actual values by more than 10 percent for ICP-OES and GFAA, 15 percent for ICP-MS and 20 percent for mercury. If values for the CCV are outside the control limits, the instrument run should be stopped, the problem corrected, the instrument recalibrated as necessary and the calibration reverified with an ICV. All samples after the last acceptable CCV must be reanalyzed.

5.6.1.5 Continuing calibration blank (CCB)

Analyze one calibration blank for every 10 samples. If the absolute value of the blank exceeds the detection limit, the analysis should be terminated, the problem corrected, the instrument recalibrated as necessary, the calibration reverified and all analytical samples after the last acceptable calibration blank reanalyzed.

5.6.1.6 ICP-OES interference check sample (ICS)

The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the interference correction factors. The ICS solutions consist of two parts; solution A contains the interferents at concentrations sufficiently high to be significant (ICSA), and solution AB contains both the interferents and the analytes at approximate concentrations of 10 times the detection limit (ICSAB). Analyze the ICSA and ICSAB in consecutive order after the ICV and before the samples. If results for the ICSAB solution fall outside the control limits of $\pm$ 20 percent of the true value, the analysis should be terminated and the problem corrected. See instrument specific reference methods for more information on how to prepare interference check samples.

5.6.1.7 GFAA Analytical Spike

The GFAA analytical spike is a second aliquot of prepared sample, spiked with the analyte of interest and analyzed exactly the same, and immediately after, the sample. The analytical spike provides information for overcoming matrix problems during analysis by graphite furnace. Most automated GFAA instruments can be programmed to perform this analysis and calculate recoveries. Control limits are 85 to 115 percent recovery, if the value of the spiked sample is 2 to 5 times the original sample concentration. Furnace programs, matrix modifiers or dilutions are adjusted to bring recoveries within these control limits. When recoveries of the instrument spike do not fall within the control limits, method of standard additions may be necessary to meet the project required detection limits.

Table 4.

Summary of Quality Control Samples for Instrument Quality Control

Analysis Type	Recommended Minimum Frequency of Analysis	Control Limits
Initial Calibration Verification (ICV)	Each instrument run, after calibration Different source from calibration standards Contains all analytes of interest	± 10% of true value for ICP-OES, ICP-MS & GFAA; ± 20% for mercury
Initial Calibration Blank (ICB)	Immediately follows ICV	absolute value < detection limit
Continuing Calibration Verification (CCV)	After every 10 samples Contains all analytes of interest	± 10% of true value for ICP-OES & GFAA, ± 15% ICP-MS; ± 20% mercury
Continuing Calibration Blank (CCB)	After every 10 samples, usually follows CCV	absolute. value < detection limit
ICP-OES Interference Check Sample (ICS)	Analyze once each instrument run, following ICV and before samples Comprised of two solutions, one containing interferents only, the other containing analytes + interferents.	± 20% of true value
GFAA Analytical Spike	Spiked second aliquot of each prepared sample Analyzed immediately after each analytical sample	85 to 115% recovery
Serial Dilution for ICP-OES/ICP-MS	Optional Indicator of possible matrix effects on analyte recovery	1:4 dilution should agree within ± 10% of original determination
Post-digestion Spike for ICP-OES/ICP-MS	Optional Typically run when matrix spike recovery is outside of control limits	75 to 125% recovery
Detection Limit Check Sample	Optional Useful in verifying analytical performance at or near detection limit	Labs should develop performance based control limits

5.6.1.8 Additional recommended instrument QC samples

The following instrument QC samples are not required but are useful to the analyst when working with complex samples and low detection limit requirements.

5.6.1.8.1 Serial dilution for ICP-OES or ICP-MS

A serial dilution is a dilution of a prepared sample (usually by a factor of 4 or 5) analyzed in the same way as the original sample. The result for the diluted sample is multiplied by the dilution factor and the product compared with the undiluted sample result. Serial dilution results are used as an indicator of possible matrix effects on analyte recovery. If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrument detection limit after dilution), analysis of a 1:4 dilution should agree within ± 10 percent of the original determination. If not, a chemical or physical interference should be suspected and corrective action taken to resolve the problem.

5.6.1.8.2 Post digestion spike for ICP-OES or ICP-MS

An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered within 75 percent to 125 percent of the known value. A post digestion spike is commonly run when the matrix spike recovery is outside of control limits. Results of a post digestion spike help to differentiate between quantification problems due to sample matrix and recovery problems due to sample digestion procedure. If the post digestion spike is not recovered within the specified limits, matrix effects may be present. If spectral interference is suspected, adjust correction factors, use an alternate wavelength or mass, or compare results with an alternate method.

5.6.1.8.3 Quantification limit check sample

A quantification limit check sample contains analytes at concentrations at or near the quantification limit and is useful in verifying method performance at or near the quantification limit. It can be taken through all the steps of the method or run only at the instrument, depending upon the goals of the laboratory. There are no recommended control limits for this check sample but laboratories should develop performance based intralaboratory control limits. Guidance on developing control limits can be found in the *EPA Handbook for Analytical Quality Control* (EPA, 1979) or Section 9.0 in the QC section of EPA methods written in the EMMC format (EPA, 1993).

5.6.2 Method Quality Control

5.6.2.1 Method Blank (MB)

A method blank is an aliquot of reagent water which is prepared and analyzed exactly like, and along with, the samples. Method blanks provide an indication of the response of the measurement system to a sample with zero concentration of analyte. In addition, method blanks provide an indication of analyte contamination that may occur during sample preparation and analysis. Method blank responses can also be used to estimate the detection limit of the measurement system, and when plotted over time, can be used to monitor the random contamination resulting from the method.

A minimum of one method blank is prepared with each batch of 20 or fewer samples. If the analyte concentration of the method blank is less than the detection limit, no corrective action is necessary. If the

analyte concentration of the method blank is greater than or equal to the detection limit and the lowest concentration of the analytes in associated samples is at least ten times the blank concentration, the results of the both the blanks and the samples are reported. If the analyte concentration of the method blank is greater than or equal to the detection limit and the lowest concentration of the analyte in the associated samples is less than 10 times the blank concentration, the source of the contamination is determined and eliminated. Affected samples should be redigested and reanalyzed. If insufficient sample is available for redigestion, the results of the blank must be reported with the sample results and the data should be qualified.

5.6.2.2 Laboratory Duplicate (LD)

A laboratory duplicate is a second aliquot of a sample, processed concurrently and identically with the original sample. Analysis of laboratory duplicate samples provides information for the determination of analytical precision for a given sample matrix. In addition, replicate analyses are useful in assessing sample homogeneity. If analytes are present in concentrations that are lower than the quantification limit, results for matrix spike duplicates and replicate check standards may be used to estimate analytical precision. One set of laboratory duplicates should be analyzed for each batch of 20 or fewer samples of the similar matrix. Relative percent difference (RPD), a commonly used means of estimating precision between duplicate analyses, is calculated using the formula:

$$RPD = 100\frac{|x_1 - x_2|}{(x_1 + x_2) / 2}$$

The recommended control limit for duplicates is ≤ 20 percent RPD if sample concentrations are greater than or equal to the quantification limit. If one sample is above the quantification limit and the other is below, the results are reported and no corrective action is taken. If both samples are less that the quantification limit, the RPD is not calculated from the laboratory duplicate results. If duplicate RPDs do not fall within control limits, the analyst should take into consideration the following: project data quality objectives, regulatory limit for the analyte, the RPD for other analytes, matrix spike and spiked blank recoveries and visual appearance of the sample (sample homogeneity). Appropriate corrective action may be redigesting and reanalyzing the sample if analytical problems are suspected. If sample homogeneity problems are suspected, the project manager should be consulted and the data may be qualified, depending upon specific project requirements as documented in the project planning document.

5.6.2.3 Matrix Spike (MS)

A matrix spike is an aliquot of sample spiked with a known concentration of analyte(s). Spiking occurs prior to sample preparation and analysis. The mean of a significant number of matrix spike results can be used to estimate bias due to matrix interference. One matrix spike should be analyzed for each batch of 20 or fewer samples of similar matrix. The spike solution is added to samples prior to digestion. The sample that is chosen for spiking should be the same sample used for laboratory duplicate analysis. A spike blank may be prepared concurrently to check spiking procedure and to provide reference for the matrix spike. The amount of spike added to the sample should be 2 to 5 times the expected sample concentration. Matrix spike recovery is calculated using the formula

$$\% \text{ Recovery} = \frac{(\text{Matrix spike sample results} - \text{unspiked sample results})}{\text{calculated spike amount}} * 100$$

Control limits for spike recovery are usually 75 to 125 percent. If the matrix spike recovery falls outside the control limits, the ratio of background concentration to calculated spike amount should be evaluated. If the sample concentration exceeds the spike concentration by a factor of 4, no corrective action is taken and the result is reported. If the factor is less than 4, corrective action is taken. The analyst should take into consideration the following: project data quality objectives, regulatory limit for the analyte, matrix or physical interferences, the duplicate RPD, matrix spike recoveries for the other analytes, spiked blank recoveries, matrix spike duplicate recoveries, known method limitations (e.g., antimony; silver) and visual appearance of the sample (sample homogeneity). A post digestion spike should be performed to provide additional information for troubleshooting analytical problems. Appropriate corrective action may be redigesting and reanalyzing the associated samples if analytical problems are suspected. Otherwise, the project manager should be consulted and the data may be qualified, depending upon specific project requirements as documented in the project planning document.

5.6.2.4 Matrix Spike Duplicate (MSD)

A matrix spike duplicate is an aliquot of sample (same sample as matrix spike) spiked with identical concentrations of analytes as the matrix spike. Results for matrix spike duplicates may be used to estimate analytical precision and may be requested by a project manager when the anticipated analyte concentrations in the samples are too low to be useful for estimating analytical precision. Calculations, control limits and corrective actions for matrix spike duplicates are consistent with those described under the sections Laboratory Duplicate and Matrix Spike, above.

5.6.2.5 Spike Dual Analysis (SDA)

A spike dual analysis is performed by analyzing a second aliquot of the matrix spike at the determinative step of the method. It may be used as an indicator of method precision when other precision indicators are not available. A spike dual analysis may be performed when low concentrations of analytes in the laboratory duplicates preclude the use of laboratory duplicate data for purposes of estimating precision and insufficient sample is available to prepare a matrix spike duplicate.

5.6.2.6 Spiked Method Blank (SB)

A spiked method blank is an aliquot of reagent water spiked at the same time and at the same concentrations as the matrix spike. It is used to check the spiking procedure. It is also useful in evaluating matrix spike results and overall method performance independent of matrix effects. Control limits are 85 to 115 percent recovery. Since the spiked method blank does not contain matrix interferences, recoveries should always be within control limits for a proven method. Corrective action for spiked method blanks that are out of control should be to investigate the cause of the problem, correct it and, if necessary, redigest and reanalyze associated samples.

5.6.2.7 Laboratory Control Sample (LCS)

A laboratory control sample is a known matrix, usually reagent water, that is spiked with analytes and processed through the entire analytical procedure. It is used to document method performance. Replicate LCS results may be used to estimate precision and the difference between the mean of those results and the true value provides an indication of the magnitude of bias due to method error. Analysis of a laboratory control sample is optional but is usually run once per analytical batch. Laboratories that routinely analyze LCSs may develop intralaboratory control limits for each analyte. Control limits should not exceed 80 percent to 120 percent of true value for a proven method. Laboratory control samples are often commercially prepared and control limits may vary, depending upon the supplier.

Table 5.

Summary of Quality Control Samples for Method Quality Control

Analysis Type	Recommended Minimum Frequency of Analysis	Control Limits
Method Blank (MB)	Minimum of one per each batch of 20 or fewer samples	< detection limit If ≥ detection limit, lowest analyte conc. must be at least 10x the MB value.
Laboratory Duplicate (LD)	One set of duplicates for each batch of 20 or fewer samples of similar matrix	≤ 20% RPD (If outside control limits and ratio of unspiked sample to spike amount is >4, no corrective action)
Matrix Spike (MS)	One matrix spike for each batch of 20 or fewer samples of similar matrix	75 to 125%
Matrix Spike Duplicate (MSD)	Optional or project specific as an estimate of analytical precision	Same as LD and MS above
Spike Dual Analysis (SDA)	Optional Analysis performed on a second aliquot of the Matrix Spike	80 to 120%
Spike Blank (SB)	Optional Reagent waster spiked at the same time and same concentrations as Matrix Spike	85 to 115%
Laboratory Control Sample (LCS)	Optional One per batch of 20 or fewer samples	80 to 120%
Reference Material (SRM/CRM)	One reference material sample for each batch of 20 or fewer samples of similar matrix	Control limits are often project specific. Recoveries may vary depending on preparation method

5.6.2.8 Reference Material

A reference material is a material containing known quantities of analytes in a homogenous matrix. An aliquot of the material is processed through the entire analytical procedure and used to document bias of the analytical method. When analyzed in duplicate, a reference material can also provide both precision and bias information for a particular matrix type.

A certified reference material (CRM) is a material that has one or more property values certified by a technically valid procedure, documented by a certifying body (e.g., National Research Council of Canada (NRCC); National Institute for Standards and Technology (NIST)). A standard reference material (SRM) is a CRM issued by the NIST.

In general, one certified or standard reference material sample is analyzed for every batch of 20 or fewer samples of a similar matrix. For mercury, one reference material sample per water bath is sufficient, even if the water bath holds more than 20 samples. Use a reference material that is as close as possible to the samples in matrix type and concentration. When evaluating analytical results of the reference material, it is helpful to know the analytical method used to determine the reference values for the analytes. For example, sediment reference material values for metals are often determined using a total digestion technique rather than a strong acid (total recoverable) digestion technique, resulting in low recoveries for some metals when using EPA Method 3050 (EPA, 1992b). A list of vendors and suppliers for reference materials can be found in Appendix A of this chapter. A laboratory can determine intralaboratory control limits for such elements based upon a minimum of seven replicate digestions and analyses. Further guidance on developing control limits can be found in the *EPA Handbook for Analytical Quality Control* (EPA, 1979) or Section 9.0 in the QC section of EPA methods written in the EMMC format (EPA, 1993). Sediment and soil reference materials are available for use with EPA Method 3050 (EPA, 1992b).

Control limits for reference materials are often project specific. It is recommended that laboratories develop intralaboratory control limits for each reference material routinely analyzed and that corrective action be based upon these performance based control limits. In addition, the analyst should take into consideration the following: project data quality objectives, regulatory limit for the analyte, matrix or physical interferences, duplicate RPDs, matrix spike recoveries, spiked blank recoveries, matrix spike duplicate recoveries and known method limitations when developing corrective actions. When the results for reference materials fall outside the project specific control limits, the project manager should be consulted and data may be qualified, depending upon specific project requirements as documented in the project planning document.

5.6.3 Control Limits

Recommended control limits for analytical QC samples are described above. Control limits that are different from these may be specified in project planning documents when appropriate. Project specific control limits must be developed in consultation with the laboratory. For example, a program may require laboratory results for an analyte that is not routinely measured and best available technology for that analyte may not be well demonstrated or documented.

5.6.4 Corrective Actions

The analyst is responsible for monitoring the analysis and troubleshooting problems as they occur. It is important to identify potential analytical problems as soon as possible so that corrective actions can be taken prior to the expiration of holding times. It is the responsibility of the laboratory to communicate analytical problems to the project manager during the analysis so that the project manager may have input into the course of corrective action. This communication is important when the laboratory is experiencing difficulty in meeting any project specific requirements, including detection limits. When reasonable corrective actions do not bring QC sample results into control, resulting data may need to be qualified, depending upon specific project requirements as documented in the project planning document. It is important for the laboratory and the project manager to agree on what constitutes reasonable corrective actions, acceptable data and the appropriate circumstances for data qualification.

6. REPORTING AND DELIVERABLES

Specific deliverable requirements must be outlined in the project planning document. Care must be taken to ensure that deliverable requirements meet project data use goals. At a minimum, the laboratory should provide a data report that includes analytical results, a tabular summary of associated QC results and control ranges, and a cover letter that references or describes the analytical procedure(s) and discusses any analytical problems. The following sections describe recommended deliverables to be included in laboratory reports.

6.1 Recommended Deliverables for Metals Analyses

- Date of analysis;
- Tabulated sample results with units, including reporting basis (e.g. wet, dry);
- Summary of digestion procedure;
- Detection limits and quantification limits;
- Method blank results for each batch of samples;
- Summary of results and control limits for all QC analyses performed by the laboratory, such as spikes, duplicates and CRMs;
- Explanations for all data qualifications;
- Reference analytical method; and
- Explanations for all departures from the analytical protocols and discussion of possible effects on the data.

6.2 Backup Documentation

All laboratories are required to submit results that are supported by sufficient quality control results and backup documentation (maintained at the laboratory) to enable independent QA reviewers to evaluate data quality and reconstruct final results from the raw data. Legible photocopies of original data sheets should be available from the laboratory with sufficient information to unequivocally identify the following items:

- calibration results;
- method blanks;
- samples, sample sizes and dilution factors;
- replicates and spikes, including amount spiked;
- control or reference samples;
- chain of custody and sampling records; and
- any anomalies in instrument performance or unusual instrument adjustments.

7. GLOSSARY

Accuracy - The agreement between an analytical result and the true value.

Ambient Water- Waters in the natural environment (e.g., rivers, lakes, streams, oceans and other receiving waters), as opposed to effluent discharges.

Analyte - That which is identified and quantified in the process of analyzing samples.

Analytical Spike - A duplicate aliquot of a prepared sample, fortified with the analyte of interest and analyzed exactly the same as, and immediately after the unspiked sample. Used with GFAA analyses to provide information for overcoming matrix related interferences.

Aqua Regia - One part of nitric acid and three parts of hydrochloric acid; used chiefly to dissolve metals.

Batch - The number of samples that are prepared or analyzed with associated laboratory QC samples at one time. A typical batch size is 20 samples.

Bias - The systematic or persistent distortion of a measurement process which causes errors in one direction.

Calibration - The determination of the relationship between analytical response and concentration (or mass) of the analyte.

Capsule Filter - A flow-through filter assembly that is self-contained, permanently assembled and disposable. The filter assembly contains filter media of a defined porosity in a configuration resulting in a large surface area.

Certified Reference Material - A reference material accompanied by, or traceable to, a certificate stating the concentration of chemicals contained in the material. The certificate is issued by an organization, public or private, that routinely certifies such material [e.g., National Research Council of Canada, American Society for Testing and Materials (ASTM)]).

Check Standard - A QC sample prepared independently of calibration standards, analyzed exactly like the samples and used to estimate analytical precision and indicate bias due to calibration.

Chelation - Formation of a heterocyclic compound having a central metallic ion attached by covalent bonds to two or more nonmetallic atoms in the same molecule.

Cold Vapor Atomic Absorption Spectroscopy - A technique for the analysis of mercury, whereby mercury is selectively chemically reduced to an elemental state and aerated from solution in a closed system. Absorption of the vapor at a given wavelength is a measure of the concentration of mercury in the sample.

Coefficient of Variation - The standard deviation expressed as a percentage of the mean. Also termed relative standard deviation or RSD.

Comparability - An indication of the confidence with which one sample result or one data set can be compared to another sample result or data set.

Continuing Calibration Blank - A volume of reagent water acidified with the same amounts of acids as were the standards and samples for a particular analysis. Used to assure absence of contamination during an analytical run.

Continuing Calibration Verification - A sample used to assure calibration accuracy during each analysis run. It must be run for each analyte as described in the particular analytical method. At a minimum, it should be analyzed at the beginning of the run and after the last analytical sample.

Control Limit(s) - A value or range of values against which results of QC sample analyses are compared in order to determine whether the performance of a system or method is acceptable. Control limits are typically statistically derived. When QC results exceed established control limits, appropriate corrective action should be taken to adjust the performance of the system or method.

Coprecipitation - The precipitation of an otherwise soluble substance along with an insoluble precipitate.

Corrective Action - Measures taken to remove, adjust, remedy or counteract a malfunction or error so that a standard or required condition is subsequently met.

Data Quality Objectives - Data quality objectives are qualitative and quantitative statements that define the appropriate type and quality of data needed to support the objective of a given project.

Dissolved Fraction - The concentration of metals contained in a sample after the sample is filtered through a 0.45 µm filter.

Duplicate Analysis - Analysis performed on a second subsample in the same manner as the initial analysis, used to provide an indication of measurement precision.

Flame Atomic Absorption Spectroscopy - A technique for metals analysis in which a sample is aspirated and atomized in a flame through which light of a prescribed wavelength is directed. The amount of light from the light beam that is absorbed by the flame is a measure of the concentration of metal in the sample.

Graphite Furnace Atomic Absorption Spectroscopy - A technique for metals analysis in which a sample is atomized in a graphite tube in a furnace, and the resulting vapor placed in a beam of radiation containing excited molecules of the element to be measured. Attenuation of the transmitted radiation is a measure of the concentration of that element in the sample.

Guideline - A suggested practice that is non-mandatory.

Holding Time - The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are used.

Inductively Coupled Argon Plasma Mass Spectrometry - A technique for multi-element analysis at relatively low concentrations. When nebulized samples are introduced into a radio frequency inductively coupled argon plasma, ions are produced. The positively charged ions are transmitted by a quadrapole mass filter, based upon selected mass to charge ratios, and isotope-specific mass spectra are produced.

Inductively Coupled Argon Plasma Optical Emission Spectroscopy - A technique for simultaneous or rapid sequential analysis for many elements in a short time. Element-specific atomic-emission line spectra of nebulized samples are produced by a radio-frequency inductively coupled plasma.

Initial Calibration Blank - A blank run immediately after the ICV standard to verify the absence of carry-over contamination.

Initial Calibration Verification Standard - A certified or independently prepared solution used to verify the accuracy of the initial calibration of an instrument.

Interelement Correction - Correcting an analytical result for the contribution to the measured concentration by interelement interferences.

Interelement Interferences - Interference caused by overlapping spectral lines of 2 or more elements, at the analytical or background measurement wavelengths (ICP-OES analyses).

Interference Check Sample - A sample run by ICP-OES methodology to verify the accuracy of interelement and background correction factors.

Integration - Calculation of the definite integral of a mathematical function. In instrumental analysis, integration is typically the means to interpret geometrically the area of a region under a curve and bounded by a set of limits on the x-axis, or a means to transform raw instrument output to calculated values.

Internal Standard - A standard added in a known amount to a sample at some stage of analysis in order to determine the concentration of analyte from the analyte response relative to the internal standard.

Interstitial Water - Water contained between the particles of soil or sediment.

Laboratory Control Sample - A known sample, usually prepared and certified by an outside agency, which is carried through the preparation and analysis procedures as if it were a sample. Replicate LCS results may be used to estimate precision and the difference between the mean of those results and the true value provides an indication of the magnitude of bias due to method error.

Linear Range - The concentration range over which the instrument calibration curve remains linear.

Major Elements - Elements which are commonly present in easily measured concentrations in a given matrix. Major metals in sea water include calcium, magnesium, potassium and sodium.

Matrix - The sample material in which the analytes of interest are found (e.g., water, sediment, tissue).

Matrix Spike - A QC sample created by adding known amounts of analytes of interest to an actual sample, usually prior to extraction or digestion. The matrix spike is analyzed using normal analytical procedures. The percent recovery is calculated as the difference between spiked and unspiked sample analysis results divided by the amount spiked and multiplied by 100. This provides an indication of sample matrix effect on recovery of target analytes.

Membrane Filter - A thin, pliable filter, typically designed to contain uniform pores of a specified dimension. Examples of membrane filter materials include polycarbonate, cellulose acetate and cellulose nitrate.

Method - A set of written instructions specifying an analytical procedure to be followed by an analyst in order to obtain a numerical estimate of the concentration of an analyte in each of one or more samples.

Method Blank - A QC sample intended to determine the response at zero concentration of analyte. A clean matrix (generally water) known to be free of target analytes that is processed through the analytical procedure in the same manner as associated samples.

Method Detection Limit - The minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero; determined from analysis of a sample in a given matrix containing the element.

Method of Standard Additions - A method of calibration and analysis that is used when interferences due to matrix effects during instrumental analysis are severe and cannot be overcome and when the interferences are proportional to the concentration of analyte. The addition of three increments of a standard solution (spikes) to three sample aliquots of the same size are made. Measurements are made on the original and after each addition. A calibration curve is constructed and, the analyte concentration is determined by the absolute value of the x-intercept of the curve.

Metro - King County Water Pollution Control Division Environmental Laboratory.

Nebulization - Transformation of a liquid sample to an aerosol.

Particulate Fraction - The concentration of metals in the portion of a sample that is retained by a 0.45 μm filter.

Post Digestion Spike - A portion of a prepared sample or its dilution is spiked with the analyte of interest and analyzed exactly the same as the unspiked sample. It provides an indication of problems which are matrix related rather than related to the efficiency of the digestion procedure.

Precision - The statistical agreement among independent measurements determined from repeated applications of a method under specified conditions. Usually expressed as RPD, RSD or coefficient of variation.

Preconcentration - The technique for enhancing the concentration of analytes in a matrix prior to sample treatment steps prescribed by the determinative method.

Project - An organized set of activities within a program.

Quality Assurance - An integrated system of management activities involving planning, implementation, assessment, reporting and quality improvement to ensure that a process, item or service is of the type and quality needed and expected by the customer.

Quality Control - The routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurement process. Quality Control is an element of quality assurance. QC samples and auditing/assessment are common quality control activities.

Qualified Data - Data to which data qualifiers have been assigned. Data qualifiers provide an indication that a performance specification in the qualified sample or an associated QC sample was not met.

Quantitation - The process of calculating the value of an analyte in a particular sample.

Quantification Limit Check Sample - A check sample containing target analytes at concentrations at or near the quantification limit; used to verify routine method performance at the quantification limit.

Reagent Grade - Analytical Reagent (AR) grade, ACS (American Chemical Society) reagent grade, and reagent grade are synonyms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

Reagent Water - Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

Reductive Precipitation - A method of separating certain elements by precipitation, using a reducing agent in the chemical reaction.

Reference Material - A material of known analyte composition which can be used for comparison of analytical results. The reported analyte concentrations have not been certified (see Certified Reference Material).

Relative Percent Difference - Difference of two measurements x_1 and x_2, divided by the mean of the measurements, multiplied by 100.

Relative Standard Deviation - see coefficient of Variation.

Replicate - One of several identical experiments, procedures, or samples.

Serial Dilution - A dilution series in which a given sample is sequentially and incrementally diluted.

Spike - The addition of a known amount of a substance to a sample or a blank.

Spiked Blank - See Check Standard.

Spiked Dual Analysis - A second aliquot of the matrix spike is analyzed at the determinative step of the method. Used as an indicator of method precision and bias due to sample matrix.

Standard - A substance or material, the properties of which are believed to be known with sufficient accuracy to permit its use to evaluate the same property of a sample. In chemical measurements, standard often describes a solution of analytes used either for calibration (calibration standard) or to check the precision of analysis (check standard).

Standard Reference Material - A material with known properties produced and distributed by the U. S. National Institute of Standards and Technology (NIST).

Trace Metals - Elements which are present in a matrix at trace concentrations; e.g. trace metals in sea water include arsenic, cadmium, chromium, copper, lead, nickel, and silver.

8. REFERENCES

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APHA, 1992b. *Standard Methods for the Examination of Water and Wastewater.* Greenberg, A.E., Clesceri, L.S., and Eaton A.D., Eds.. 18th ed., Part 3000, Method 3030A, p 3-3. American Public Health Association, Washington, DC.

ASTM, 1995a. *Annual Book of ASTM Standards. Section 11: Water and Environmental Technology*. Furcola, N.C., Gutman, E.L., Kauffman, S.L., Kramer, J.G., Leinweber, C.M., Mayer, V.A., McGee P.A., Eds., Vol. 11.02 (Water II), D5074-90 (Reapproved 1992), pp 687-691. American Society for Testing and Materials, Philadelphia, PA.

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EPA, 1979. *Handbook for Analytical Quality Control in Water and Wastewater Laboratories*. EPA-600/4-79-019. U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati OH.

EPA, 1991a. Method 245.5. *Determination of Mercury in Sediment by Cold Vapor Atomic Absorption Spectrometry.* EPA /600-4-91/010. Office of Research and Development, Washington DC.

EPA, 1991b. Method 200.3. *Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements in Biological Tissues*. EPA/600-4-91/010. Office of Research and Development, Washington, DC.

EPA, 1991c. Method 245.6. *Determination of Mercury in Tissues by Cold Vapor Atomic Absorption Spectrometry.* EPA/600-4-91/010. Office of Research and Development, Washington, DC.

EPA, 1992a. Method 200.10. *Determination of Trace Elements in Marine Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma - Mass Spectrometry*. EPA/600/R-92/121. Office of Research and Development, Cincinnati, OH.

EPA, 1992b. Method 3050. *Test Methods for Evaluating Solid Waste. Laboratory manual physical/chemical methods.* SW-846, 3rd ed., Vol. IA, Chapter 3, Sec 3.2, Rev 1. Office of Solid Waste and Emergency Response, Washington, DC.

EPA, 1992c. Method 200.13 [Cd, Cu, Pb]. *Determination of Trace Elements in Marine Waters by Off-Line Chelation Preconcentration with Graphite Furnace Atomic Absorption.* EPA/600/R-92/121. Office of Research and Development, Cincinnati, OH.

EPA, 1992d. Method 200.12. *Determination of Trace Elements in Marine Waters by Stabilized Temperature Graphite Furnace Atomic Absorption*. EPA/600/R-92/121. Office of Research and Development, Cincinnati, OH.

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EPA, 1994b. *Monitoring Trace Metals at Ambient Water Quality Criteria Levels: Issues, Plans and Schedule.* Office of Water, Office of Science and Technology Engineering and Analysis Division, Washington, DC.

EPA, 1994c. Method 200.7. *Determination of Metals and* Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry. EPA/600/R-94/111. Office of Research and Development. Washington, DC.

EPA, 1994d. Method 200.8. *Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma-Mass Spectrometry.* EPA/600/R-94/111. Office of Research and Development, Washington, DC.

EPA, 1994e. Method 245.1. *Determination of Mercury in Water by Cold Vapor Atomic Spectrometry* EPA/600/R-94/111. Office of Research and Development, Washington, DC.

EPA, 1994f. Method 245.7. *Determination of Mercury by Automated Cold Vapor Atomic Fluorescence Spectrometry*. EPA/600/R-94/111. Office of Research and Development, Washington, DC.

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EPA, 1995a. *Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities*. 821-B-95-001,

Draft. Office of Research and Development, Washington, DC.

EPA, 1995b. Method 1669. *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*. EPA-R-95-034. Office of Water, Washington, DC.

EPA, 1995c. Method 1631. *Mercury in Water by Oxidation, Purge and Trap, Cold Vapor Atomic Fluorescence Spectrometry*. EPA-821-R-95-027, **Draft**. Office of Water Engineering and Analysis Division, Washington, DC.

EPA, 1995d. Method 1632. *Determination of Inorganic Arsenic in Water by Hydride Generation flame Atomic Absorption.* EPA-821-R-95-028, **Draft**. Office of Water Engineering and Analysis Division, Washington, DC.

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PSEP, 1990. *Recommended Protocols for measuring Conventional Water Quality Variables and Metals in Fresh Water of the Puget Sound Region*. Prepared for U.S. Environmental Protection Agency Region 10, Office of Puget Sound, Seattle, WA. Tetra Tech, Inc., Bellevue, WA.

PSEP, 1997a. *Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound*. Prepared for U. S. Environmental Protection Agency Region 10, Office of Puget Sound, Seattle, WA and Puget Sound Water Quality Action Team, Olympia, WA. King County Environmental Laboratory, Seattle, WA.

PSEP, 1997b. *Recommended Quality Assurance and Quality Control Guidelines for the Collection of Environmental Data in Puget Sound.* Prepared for U. S. Environmental Protection Agency Region 10, Office of Puget Sound, Seattle, WA and Puget Sound Water Quality Action Team, Olympia, WA. King County Environmental Laboratory, Seattle, WA.

PSEP, 1997c. *Recommended Guidelines for Measuring Organic Compounds In Puget Sound Water, Sediment and Tissue Samples. Section* 5.3.2, pp 10-11. Prepared for U. S. Environmental Protection Agency Region 10, Office of Puget Sound, Seattle, WA and Puget Sound Water Quality Action Team, Olympia, WA. King County Environmental Laboratory, Seattle, WA.

Taylor, T.E. and Shiller, A.M., 1995. *Mississippi River Methods Comparison Study: Implications for Water Quality Monitoring of Dissolved Trace Elements.* Environ. Sci. Technol., 29:1313-1317.

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9. APPENDIX A: SUPPLIERS OF REFERENCE MATERIALS

Table A-1

Metal Analysis SRM and CRM Materials

Reference Material	Source	Name and Matrix
1646a	NIST	Estuarine Sediment
2704	NIST	Buffalo River Sediment
2709	NIST	San Joaquin Soil, Baseline
2710	NIST	Montana Soil High, Traces
2711	NIST	Montana Soil Moderate, Traces
1643d	NIST	Trace Metals in Water (spiked dilute nitric acid)
BCSS-1	NRCC	Coastal Marine Sediment
MESS-2	NRCC	Estuarine Sediment
PACS-1	NRCC	Harbour Sediment
DORM-2[a]	NRCC	Dogfish Liver
DOLT-2[a]	NRCC	Dogfish Muscle
TORT-2[a]	NRCC	Lobster Hepatopancreas
LUTS-1[a]	NRCC	Nondefatted Lobster Hepatopancreas
CASS-3	NRCC	Nearshore Seawater
NASS-4	NRCC	Open Ocean Seawater
SLEW-2	NRCC	Estuarine Water

Notes:

[a] Certified for methyl mercury.

Please note that most of the certified values for the SRM and CRM material listed in the tables were generated using either Total (complete) digestion techniques or nonstandard extraction techniques. As a result, certified values may not be directly comparable with extraction techniques used in most laboratories. This must be kept in mind when using this information to qualify or validate the generation of sediment, tissue and water data. NIST soil SRMs have data available that have been determined by EPA Method 3050 (EPA, 1992). The values are not certified but are usable for information only.

SRM and CRM Vendors

National Institute of Standards and Technology (NIST)
Standard Reference Materials Program
Room 204, Building 202
Gaithersburg, MD 20899-0001
Phone: (301) 975-6776 FAX: (301) 948-3730
e-mail: SRMINFO@enh.nist.gov
NIST provides soil, sediment and water (no seawater) SRMs.

National Research Council of Canada (NRCC)
Institute for Environmental Research and Technology
Ottawa, Ontario, Canada K1A 0R6
Phone: (613) 993-2359 FAX: (613) 993-2451
e-mail: crm.iert@nrc.ca
NRCC provides marine materials, including seawater, marine sediments and marine tissues.

Resource Technology Corporation (RTC)
P. O. Box 1346
2931 Soldier Springs Road
Laramie, WY 82070
Phone: (307) 742-5452 FAX: (307) 745-7936
RTC is both a producer and distributor of CRM and SRM materials. They handle materials from the EPA, NRCC, Europe and Asia.

Environmental Resource Associates (ERA)
5540 Marshall Street
Arvada, CO 80002
Phone: 1-800-372-0122 FAX: (303) 421-0159
ERA distributes a variety of quality control standards, including a Metals in Soil standard with values determined by EPA Method 3050 (EPA, 1992).

9.1 References for Appendix A

EPA, 1992. Method 3050. *Test Methods for Evaluating Solid Waste. Laboratory manual physical/chemical methods.* SW-846, 3rd ed., Vol. IA, Chapter 3, Sec 3.2, Rev 1. Office of Solid Waste and Emergency Response, Washington, DC.

10. APPENDIX B: METHOD REFERENCES FOR METHYL MERCURY

At this time there are no EPA methods for the analysis of methyl mercury. Following are references for analysis of methyl mercury in marine samples.

Bloom, N.S., 1989. *Determination of picogram levels of methyl mercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection.* Can. J. Fish. Aquat. Sci., 46:1131-1140.

Bloom, N.S., 1992. *On the chemical form of mercury in edible fish and marine invertebrate tissue.* Can. J. Fish. Aquat. Sci., 1992, 49:1010-1017.

Horvat, M., Bloom, N.,S. and Liang, L., 1993. *Comparison of distillation methods for the determination of methyl mercury compounds in low level environmental samples. Part I. Sediments* . Analytica Chimica Acta 1993, 281:135-152.

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Liang, L., Horvat, M. and Bloom, N.S., 1994. *Simultaneous determination of mercury speciation in biological materials by GC/CVAF after ethylation and room-temperature precollection*. Clin. Chem., 40/4, 602-607.

Bloom, N.S. and Von Der Geest, E.J. 1992. *Matrix modification to improve the recovery of MMHg from clear water using distillation.* Water, Air, and Soil Pollution, 80:1319-1323.

11. APPENDIX C: ACID VOLATILE SULFIDE AND SIMULTANEOUSLY EXTRACTED METALS

11.1 Introduction

The toxicity of chemicals in sediments is influenced by the extent that chemicals bind to the sediment. It has been shown that the bioavailability of some metals in sediment is influenced by the presence of sulfide, as some metals can form insoluble sulfides. Acid volatile sulfide (the solid phase sediment sulfides that are soluble in cold acid) is a reactive pool of solid phase sulfide that is available to bind with metals. In the development of sediment criteria, EPA has proposed accounting for the mitigating impact of sulfides present in sediment by using the ratio of metals concentrations, as simultaneously extracted metals (SEM), to acid volatile sulfide concentrations (AVS). Metals that are thought to be influenced by AVS are cadmium, copper, lead, mercury, nickel, and zinc. Ecology's Sediment Quality Standards (SQS) are based upon observed effect to aquatic life, and therefore, the AVS/SEM measurement is not used in the sediment cleanup or source control programs.

11.2 Method of Analysis

EPA has published the method *Analytical Method for Determination of Acid Volatile Sulfide and Selected Simultaneously Extractable Metals in Sediment* (EPA, 1991). The method describes procedures for the determination of acid volatile sulfide (AVS) and for selected metals that are solubilized during the acidification step (simultaneously extracted metal, SEM). The method uses the same conditions for release of both sulfide and metal from the sediment and thus provides a useful means of assessing the amount of metal associated with sulfide.

There are some important practical considerations with using the AVS/SEM Method. First, the hydrochloric acid reagent used to acidify the samples may have an impact on the subsequent determinative methods for the SEM. The hydrochloric acid reagent causes formation of chlorides in the SEM fraction. Chlorides are known to interfere with analysis of some elements by GFAA and ICP-MS (EPA, 1992 and EPA, 1994). The AVS/SEM method specifies analysis of the SEM fraction by ICP-OES or atomic absorption (AA) but does not provide a distinction between FLAA and GFAA. It is important to recognize this limitation and that detection limits below those achievable by ICP-OES may not be feasible. Additional information about AVS/SEM methods can be found in the following references.

11.3 References for Appendix C

Allen, H.E, Fu, G, Boothman, W, DiToro, D.M. and Mahony, J.D., 1992. A*nalytical method for determination of acid volatile sulfide and selected simultaneously extracted metals in sediment.* December 2, 1991. Prepared for U. S. Environmental Protection Agency, Office of Water, Washington, DC.

DiToro, D.M., Mahony, J.D., Hansen, D.J., Scott, K.J., Hicks, M.B., Mayr, S.M. and Redmond, M.S., 1990. *Toxicity of cadmium in sediments: the role of acid volatile sulfide.* Environmental Toxicology and Chemistry, Vol. 9, pp 1487-1502.

EPA, 1991. *Analytical Method for Determination of Acid Volatile Sulfide and Selected Simultaneously Extractable Metals in Sediment.* December, 1991. Office of Water, Office of Science and Technology Health and Ecological Division, Washington, DC.

EPA, 1992. Method 200.12. *Determination of Trace Elements in Marine Waters by Stabilized Temperature Graphite Furnace Atomic Absorption*. EPA/600/R-92/121. Office of Research and Development, Cincinnati, OH.

EPA, 1994. Method 200.8. *Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma-Mass Spectrometry.* EPA/600/R-94/111. Office of Research and Development, Washington, DC.

Lasorsa, B. and Casas, A., 1994. *A comparison of sample handling and analytical methods for determination of acid volatile sulfides in sediment.* June, 1994. Battelle Marine Sciences Laboratory, Sequim, WA., University of Washington School of Fisheries, Seattle, WA.

12. APPENDIX D: ALTERNATE METHODS FOR THE ANALYSIS OF MARINE WATER SAMPLES, AS COMPARED WITH THE VALIDATED METHODS.

Section 5.3.4 of this chapter includes validated methods for the analysis of marine water samples. When projects require lower detection limits or analytes that are not included in these methods, the use of non-validated analytical methods may be necessary to meet project requirements. This appendix summarizes some methods described in the literature for analysis of trace elements in sea water at low levels.

12.1 Chelation

Chelation procedures offer the ability to concentrate analytes of interest while at the same time removing undesirable sample constituents from the sample matrix. One drawback of this approach is that no one chelation chemistry has been found to be applicable to all of the analytes commonly of interest. The EPA published preconcentration methods are based on iminodiacetate (IDA) resins and are applicable to cadmium, copper, lead, and nickel. The 8-hydroxyquinoline (8HOQ)-based resins provide similar performance for the same list of analytes. Zinc is also amenable to both of these chemistries, but contamination impacts detection limits. Another chemistry, based on ammonium pyrolidine dithiocarbamate (APDC), has been proposed for antimony and selenium. No chelation procedures are offered here for chromium or thallium. Chelation procedures often have applicability to analytes other than those specified in the EPA Marine Water Quality Criteria (Table 1, Section 5.3.3), and specific information about these analytes can be found in the referenced methods. A discussion of specific chelation procedures follows.

12.1.1 Iminodiacetate / On- or Off-Line / Spectrometric Determination

The preconcentration techniques that are based on iminodiacetate resins are limited in scope but may be automated or semi-automated. Both on- and off-line variations have been published by the EPA and pre-assembled iminodiaceatate chelation units are commercially available. The off-line technique currently published for use with GFAA (EPA 200.13 (EPA, 1992a)) could, in principle, also be applied to ICP-OES and ICP-MS. However, a limited sample volume is produced by the chelation units and sample volume requirements for ICP-OES and ICP-MS would need to be addressed. The iminodiacetate methods are applicable to analysis of cadmium, copper, lead, and nickel. The chelation chemistry is appropriate for zinc, but zinc detection limits have been severely limited by contamination. The method is also applicable to a number of other elements than those listed in the EPA Marine Water Quality Criteria.

- **Iminodiacetate / Off-Line / GFAA**

  EPA Method 200.13 *Determination of Trace Elements in Marine Waters by Off-Line Chelation Preconcentration with Graphite Furnace Atomic Absorption* (EPA, 1992a).

  EPA Method 1637 *Determination of Trace Elements in Ambient Waters by Chelation Preconcentration with Graphite Furnace Atomic Absorption* (EPA, 1995a, Draft).

The two off-line GFAA methods are procedurally very similar. EPA 200.13 (EPA, 1992a) is applicable to cadmium, cobalt, copper, lead, and nickel while EPA Method 1637 (EPA, 1995a, **Draft**) is applicable

to only cadmium and lead. EPA Method 1637 (EPA, 1995a, **Draft**) is a performance based method that is based on Method 200.13 (EPA, 1992a) but includes extensive use of clean room technology and QA/QC to verify cleanliness and method performance. Both methods are automated or semi-automated, off-line procedures. Detection limits for EPA Method 200.13 (EPA, 1992a) were determined using the NRCC reference material NASS-3. These detection limits are lower than the EPA Marine Water Quality Criteria. EPA Method 1637 (EPA, 1995a, Draft) does not clearly state if the detection limits reported were determined with deionized water blanks or synthetic sea water blanks but, since the two procedures are so similar, they could be expected to perform similarly.

- **Iminodiacetate / On-Line / ICP-MS**

  EPA Method 200.10 *Determination of Trace Elements in Marine Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma - Mass Spectrometry* (EPA, 1992b).
  EPA Method 1640 *Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma - Mass Spectrometry* (EPA, 1995b, Draft).

The two on-line ICP-MS preconcentration methods are procedurally very similar. EPA Method 200.10 (EPA, 1992b) is applicable to cadmium, cobalt, copper, lead, nickel, uranium, and vanadium while EPA Method 1640 (EPA, 1995b, Draft) is applicable to only cadmium, copper, lead, and nickel. EPA Method 1640 (EPA, 1995b, Draft) is a performance based method that is based on EPA Method 200.10 (EPA, 1992b) but includes extensive use of clean technology and QA/QC to verify cleanliness and method performance. Both methods are automated or semi-automated, on-line, procedures. The detection limits given in methods 200.10 (EPA, 1992b) and 1640 (EPA, 1995b, Draft) were determined with reagent blanks. While the detection limits reported in the method are lower than EPA Marine Water Quality Criteria, method performance with actual sea water samples may yield higher detection limits.

- **Iminodiacetate / On-Line / ICP-OES**

  Rowan, J.T., Prell, L.J., Dobb, D.E. and Heithmar, E.M., 1990. *Trace Element Preconcentration Applied to Inductively Coupled Plasma Atomic Emission Spectrometry*. EPA Project Report 600/X-91/086. Prepared for U. S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

This on-line ICP-OES preconcentration procedure is very similar to the above ICP-MS procedure and the analyte list is the same. A commercial version of the apparatus for doing on-line ICP-OES has been available for some time. Variations between the ICP-OES and ICP-MS procedures result primarily from differences in data acquisition methods. The technique demonstrates a number of limitations that still need to be addressed. Principal among these is the transient nature of the signal which makes conventional background corrections difficult. Carry-over is also a problem for some analytes.

Table D-1
Summary of Pretreatment Methods and Reported Detection Limits (µg/L) for Analysis of Metals in Sea Water

	Chelation				Precipitation			
	IDA/On-Line[a,b,‡] (200.10/1640)	IDA/Off-Line[c,i] (200.13/1637)	8-HOQ[a] On-Line	APDC/C18[d,i] Off-Line	Reductive PPT w/ $NaBH_4$		Co-PPT w/ Cobalt APDC[g]	Co-PPT w/ Gallium[h]
	ICPMS	GFAA	ICPMS	GFAA	ICPMS[e,§]	GFAA[f,§]	GFAA	ICPMS
Sample (mL)	5	10	5	300-400	1000	900	200	200
Conc. Factor	~5	~10	~5	75-100	10	36	40	10
Antimony	N/A	N/A	N/A	0.06	**0.009**	0.004	N/A	N/A
Arsenic	N/A	N/A	N/A	Potential	0.1	0.019	N/A	0.0015
Cadmium	0.0025	0.016	0.0003	Potential	0.009	0.001	0.012	0.0022
Chromium	N/A	N/A	N/A	N/A	0.1	0.0013	N/A	0.002
Copper	0.0024	0.36	0.0020	Potential	**0.04**	0.007	0.02	0.0025
Lead	0.0016	0.28	0.0011	Potential	0.02	0.0003	0.019	0.0021
Mercury	N/A	N/A	N/A	N/A	**0.009**	N/A	N/A	N/A
Nickel	0.0545	-	0.0028	Potential	0.05	0.006	0.051	0.0009
Selenium	N/A	N/A	N/A	0.009	0.05	**0.002**	N/A	N/A
Silver	N/A	N/A	N/A	N/A	0.005	0.0007	0.0511	N/A
Thallium	N/A	N/A	N/A	N/A	0.009	0.011	N/A	N/A
Zinc	0.0360	N/A	0.0083	Potential	0.3	0.003	N/A	0.0061

Notes on shading:	<90% Recovery	**<80% Recovery**

Notes:

a. Detection limit based on 3σ0.1M HNO_3 blank (5 mL sample) (McLaren et al., 1993).
b. **EPA Method 200.10** *Determination of Trace Elements in Marine Waters by On-Line Chelation Preconcentration and Inductively Coupled-Mass Spectrometry* (EPA, 1992b).
c. **EPA Method 200.13** *Determination of Trace Elements in Marine Waters by Off-Line Chelation Preconcentration with Graphite Furnace Atomic Absorption* (EPA, 1992a).
d. Detection limits are based upon standard deviation of determinations on actual samples (300 mL) with concentrations near the detection limit (Sturgeon et al., 1985).
e. *Analyzing Sea Water by ICP - MS* (Christian, 1993).
f. *Determination of Trace Elements in Sea Water by Graphite-Furnace Atomic Absorption Spectrometry After Preconcentration by Tetrahydroborate Reductive Precipitation* (Nakashima, 1988).
g. Copper and lead detection limits determined in sea water matrix. Silver, cadmium, and nickel detection limits determined in reagent water with no spike recovery data available (Falke and Bloom, 1996).
h. The detection limits were determined for preconcentrated aqueous standards, but not with sea water standards (Sawatari et al., 1995).
i. Detection limit determined by spiking NASS-3 with metals.
‡ Detection limit from source other than the method.
§ Method of determining detection limits is not clear.
N/A The method is either not applicable or has not been demonstrated to be applicable to this analyte.
PPT Precipitation

12.1.2 Silica Immobilized 8 - Hydroxyquinoline (8-HOQ)/On-line ICP-MS

McLaren, J.W.; Lam, J.W.H., Berman, S S.; Akatsuka, K.; Azeredo, M.A., 1993. *On-line Method for the Analysis of Sea Water for Trace Elements by Inductively Coupled Plasma-Mass Spectrometry* Journal of Analytical Atomic Spectroscopy, 8:279-286 (McLaren et al., 1993).

Seubert, A.; Petzold, G.; McLaren, J.W., 1995. *Synthesis and Application of an Inert Type of 8-Hydroxyquinoline-Based Chelating Ion Exchanger for Sea Water Analysis Using On-line Inductively Coupled Plasma-Mass Spectrometry Detection* . Journal of Analytical Atomic Spectroscopy, 10:371-379 (Seubert et al., 1995).

This on-line ICP-MS preconcentration method is procedurally very similar to the iminodiacetate methods. The column, reagents and pH of the chelation chemistry are different, but the same apparatus can be used and the analyte list is the same as for the iminodiacetate method. The chelating resin is not commercially available, however, and must be synthesized in the laboratory. Consistent performance of the chelating resin depends upon successful and consistent synthesis of this material, which may be a limiting factor in the success of the method. It is an automated or semi-automated, on-line procedure. The detection limits given in Table D-1 are lower than the EPA Marine Water Quality Criteria (EPA, 1994) but were determined with deionized water blanks rather than sea water blanks and therefore may not be a realistic estimate of what individual laboratories would achieve for marine samples. It is important to note, however, that nonmatrix matched standards were used for the quantitation of marine water CRMs with good results. Seubert, et al. discuss some further developments in the 8-HOQ resin material and in the methodology that may provide further improvements in the method performance.

12.1.3 APDC / C-18 Silica Gel Adsorption / Off-Line GFAA

Sturgeon, R.E.; Willie, S.N.; Berman, S.S., 1985. *Preconcentration of Selenium and Antimony from Sea water for Determination by Graphite Furnace Atomic Absorption Spectrometry.* Anal. Chem., 57:6-9 (Sturgeon et al., 1985).

This is an off-line preconcentration method specifically for selenium and antimony. APDC is added to the acidified sample prior to column injection. The sample is loaded onto a C-18 bonded silica gel column in which the chelated metals are adsorbed. Adsorbed metal chelates are then eluted with methanol. The eluate is evaporated to near dryness and diluted with 1 percent HNO_3. Concentration factors of 200-fold are obtainable. The technique is directly applicable (includes performance data) for Sb and Se, but Se(VI) must be reduced to Se(IV) in order to determine total Se. The detection limits were based on the standard deviations of determinations on sea water CRM samples with concentrations near the detection limit. The detection limits are lower than the EPA Marine Water Quality Criteria for these two analytes. The authors report that the technique may also have application to Cd, Co, Cu, Ni, Bi, Pb, Zn, As(III), Sn(II) and V(V), but no performance data are offered.

12.2 Precipitation

Precipitation techniques are attractive as alternatives to chelation because of their broader scope, comparable detection limits and their relative freedom from complex mechanical or chromatographic apparatus. Clean room technologies are required to successfully perform these procedures and obtain the detection limits needed to meet water quality criteria. No EPA precipitation methods are available at this time. None of the precipitation methods specify a digestion step for total recoverable metals. The reference methods below are described in the literature and the reported detection limits are low enough to meet EPA Marine Water Quality Criteria (EPA, 1994).

12.2.1 Tetrahydroborate Reductive Precipitation / GFAA or ICP-MS

Nakashima, S.; Sturgeon, R.E.; Willie, S.N.; Berman, S.S., 1988 *Determination of Trace Elements in Sea Water by Graphite-Furnace Atomic Absorption Spectrometry After Preconcentration by Tetrahydroborate Reductive Precipitation*. Analytica Chimica Acta**,** 207:291-299 (Nakashima et al., 1988).

Christian, J.D. *Analyzing Seawater by ICP-MS.* Environmental Laboratory 1993, October/November, 10-13 (Christian, 1993).

A 900 to 1000 mL sample is initially acidified with nitric acid for sample preservation. The pH is then adjusted to pH 8 to 9 with ammonium hydroxide. Iron, palladium and filtered sodium tetrahydroborate ($NaBH_4$) are added and the sample and the reaction mixture is allowed to sit for 15 hours. The liquid is then filtered through a 0.45 μm filter (filters were found to be the most troublesome source of contamination). Nitric and hydrochloric acids are used to dissolve the precipitate and the solution is analyzed by GFAA or ICP-MS. A 10- to 36-fold concentration factor is realized by this method.

The reductive precipitation method is suitable for determination of more elements of interest to Puget Sound programs than any of the chelation techniques. Of interest is the technique's possible application to mercury, though the reported sea water recovery is somewhat low at 72 percent. Elements listed in the Water Quality Criteria that seem to perform well are arsenic, cadmium, chromium, lead, silver, thallium and zinc. Copper and nickel have shown low recoveries from spiked sea water but have shown good recoveries for sea water CRMs. Nakashima, et al. reported that selenium recoveries are dependent on oxidation state. Se(VI) shows good recovery in deionized water but poor recovery (approximately 15 percent) in sea water while Se(IV), seems to perform adequately in both. Selenium data, therefore, can only be expected to represent the Se(IV) in sea water.

The choice of determinative method has some influence on how the technique is performed. The use of hydrochloric acid causes isobaric interferences on arsenic and chromium by ICP-MS and concentrations of HCl must be minimized when analyzing for these elements. If arsenic and chromium are not required, greater preconcentration factors can be realized. The high levels of palladium can cause suppression in GFAA analyses which necessitates matrix matching and the method of standard additions. ICP-OES could be used for the determinative step if project required detection limits are met.

12.2.2 Gallium Coprecipitation / ICP-MS and ICP-OES

Sawatari, H., Fujimori, E. and Haraguchi, H., 1995. *Multi-Elemental Determination of Trace Elements in Sea water by Gallium Coprecipitation and Inductively Coupled Plasma Mass Spectrometry*. Anal. Sci., 11:369-374 (Sawatari et al., 1995).

Gallium in solution, is added to 200 mL of an acid-preserved sample, and the pH is adjusted with sodium hydroxide. The optimal pH is between 9 and 10, and it may depend on the magnesium concentration in the sample. The precipitate is filtered on a 0.45 µm membrane filter and is then dissolved in nitric acid (tin requires hydrochloric acid). The sample is diluted to 20 mL to give a concentration factor of 10.

The method offers a high degree of matrix elimination and is amenable to ICP-MS and ICP-OES. Larger concentration factors are possible but may result in high levels of dissolved solids that are prohibitive for ICP-MS. Of the elements listed in the Water Quality Criteria, very good performance is reported for arsenic, chromium, lead and zinc. Recoveries from sea water samples are reported to be between 80 percent and 90 percent for copper and cadmium. The method shows poor recovery (1 percent) for antimony, and no data are offered for silver.

12.2.2.1 Cobalt Pyrrolidinedithiocarbamate Coprecipitation / GFAA

Falke, A. and Bloom, N.S., 1996. *Determination of Ag, Cd, Cu, Pb, and Ni in Water by Co-APDC Coprecipitation and ZGF-AAS Determination (FGS-032).* Frontier Geosciences 1996 QA Manual, pp 307-322 (Falke and Bloom, 1996).

Bloom, N.S. and Crecelius, E.A., 1984. *Determination of Silver in Sea Water by Coprecipitation with Cobalt Pyrrolidinedithiocarbamate and Zeeman Graphite-Furnace Atomic Absorption Spectrometry*. Analytica Chimica Acta, 156:139-145 (Bloom and Crecelius, 1984).

200 mL samples are acid-digested in dilute nitric acid and then diluted back to the original sample size. Cobalt(II) and APDC solutions are added and the sample is left to stand for one hour. The sample is filtered and the APDC complex is destroyed with a small aliquot of concentrated nitric acid. The metals are redissolved in acidic ammonium dihydrogen phosphate to a volume of five mL (40-fold concentration). The ammonium dihydrogen phosphate serves as a GFAA matrix modifier. Since GFAA requires smaller sample volumes, it can tolerate larger concentration factors (smaller final volumes) than ICP and ICP-MS.

Of the elements listed in the Water Quality Criteria (EPA, 1994), the method is applicable to silver, cadmium, copper, lead, and nickel. Copper and lead detection limit and spike recovery data were determined in a sea water matrix. Silver, cadmium, and nickel detection limits were determined in deionized water and no spike recovery data are provided. Bloom and Crecelius (Bloom and Crecelius, 1984) report that silver recoveries are better than 90 percent.

12.3 References for Appendix D

Bloom, N.S. and Crecelius, E.A., 1984. *Determination of Silver in Sea Water by Coprecipitation with Cobalt Pyrrolidine Dithiocarbamate and Zeeman Graphite-Furnace Atomic Absorption Spectrometry*. Analytica Chimica Acta, 156:139-145.

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EPA, 1994. *Monitoring Trace Metals at Ambient Water Quality Criteria Levels: Issues, Plans and Schedule.* Office of Water, Office of Science and Technology Engineering and Analysis Division, Washington, DC.

EPA, 1995a. Method 1637 [Cd, Pb]. *Determination of Trace Elements in Ambient Waters by Chelation Preconcentration with Graphite Furnace Atomic Absorption*. EPA-821-R-95-030, **Draft**. Office of Water Engineering and Analysis Division, Washington, DC.

EPA, 1995b. Method 1640. *Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma Mass Spectrometry*. EPA 821-R-95-033, **Draft**. Office of Water Engineering and analysis Division, Washington, DC.

Falke, A. and Bloom, N.S., 1996. *Determination of Ag, Cd, Cu, Pb, and Ni in Water by Co-APDC Coprecipitation and ZGF-AAS Determination (FGS-032).* Frontier Geosciences 1996 QA Manual pp 307-322.

McLaren, J.W., Lam, J.W.H., Berman, S.S., Akatsuka K. and Azeredo, M.A., 1993. *On-line Method for the Analysis of Sea Water for Trace Elements by Inductively Coupled Plasma-Mass Spectrometry*. Journal of Analytical Atomic Spectroscopy, 8:279-286.

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Rowan, J.T., Prell, L.J., Dobb, D.E. and Heithmar, E.M., 1990. *Trace Element Preconcentration Applied to Inductively Coupled Plasma Atomic Emission Spectrometry.* EPA Project Report 600/X-91/086. Prepared for U. S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

Sawatari, H., Fujimori, E., Haraguchi, H., 1995. *Multi-Elemental Determination of Trace Elements in Sea water by Gallium Coprecipitation and Inductively Coupled Plasma Mass Spectrometry*. *Anal. Sci.,* 11:369-374.

Seubert, A., Petzold, G., McLaren, J.W., 1995. *Synthesis and Application of an Inert Type of 8-Hydroxyquinoline-Based Chelating Ion Exchanger for Sea Water Analysis Using On-line Inductively Coupled Plasma-Mass Spectrometry Detection*. Journal of Analytical Atomic Spectroscopy, 10:371-379.

Sturgeon, R.E., Willie, S.N., Berman, S.S., 1985. *Preconcentration of Selenium and Antimony from Sea water for Determination by Graphite Furnace Atomic Absorption Spectrometry*. Anal. Chem., 57:6-9.

13. APPENDIX E - EPA REGION 10 LABORATORY PROCEDURE FOR DETERMINATION OF DETECTION AND QUANTITATION LEVELS FOR INORGANIC ANALYSES

DETERMINATION OF DETECTION AND QUANTITATION LEVELS FOR INORGANIC ANALYSES

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Under the technical direction of the Manchester Environmental Laboratory's Metals Section.
Edited by: Metals Section, USEPA
Revision No.: 1.2
Revision Date: 03/20/96

1.0 Scope and Application

This procedure outlines the steps necessary to determine the instrument detection limit (IDL), the method detection limit (MDL), the reliable detection level (RDL) and the practical quantitation level (PQL) for analytical instrumentation used in analysis of inorganic samples. This method follows EPA and CLP SOW guidelines, however, the exact method is unique to the metals section of the Manchester Laboratory. This procedure does not address the considerable debate and disagreement over proper terms and methodology, rather, it is meant to provide specific directions for determining and reporting detection levels for metals analyses at this laboratory facility.

2.0 Summary of Method

After initial setup and calibration of the instrument, ten reagent blank samples are analyzed consecutively. The mean and standard deviation of the ten blank sample results are calculated using 9(n-1) degrees of freedom. The IDL is determined by multiplying the standard deviation by three (3σ). A low level standard (LLS) solution is made to contain concentrations of analytes at three to five times the calculated concentration of the IDL. Seven LLS samples are analyzed consecutively and according to standard analytical and quality control procedures. The standard deviation (σ with n-1) is calculated for the seven analytical results. The estimated MDL is determined by multiplying the standard deviation times three. The LLS is analyzed in the same manner on three non-consecutive days. The final MDL is the average of the three estimated MDLs. The RDL is established above the MDL to provide a practical level of detection for routine analyses. The PQL is experimentally determined by measuring analyte concentrations progressively larger than the RDL until a series of ten measurements demonstrates percent relative standard deviation of less than or equal to 10% and accuracy of the mean should be within 90 - 110% of the true value.

3.0 Procedure

3.1 Initial instrument set up.

3.1.1 Set up the instrument according to the manufacturer's guidelines. Establish interference and background correction factors.

3.2 Determine the instrument detection limit (IDL).

3.2.1 Definition: The IDL is the constituent concentration that produces a signal greater than three standard deviations of the mean noise level.

3.2.2 Calibrate the instrument according to CLP and Laboratory guidelines.

3.2.3 After calibration, run initial quality control standards at CLP or Laboratory established limits as verification. Analyte concentrations should be within 90% - 110% of the known value for ICP-AES, ICP-MS; GFAAS, and FAAS analyses, 80% - 120% for CVAAS (mercury).

3.2.4 Analyze a blank solution to determine that no carryover is present in the system.

3.2.5 Prepare a high purity reagent blank solution which matches the routine sample to be analyzed by the analytical instrument.

3.2.6 Transfer the reagent blank solution to ten clean analytical containers. Treat each container as a unique, separate sample.

3.2.7 For instruments that aspirate or sparge a sample continuously:

3.2.7.1 Introduce the sample to the system and allow the aspiration or sparge to equilibrate.

3.2.7.2 Analyze a reagent blank using the same length and number of integrations and replications as is used in the routine analysis of samples.

3.2.7.3 Flush the system after each analysis according to normal operating procedures.

3.2.7.4 Repeat this procedure for the remaining reagent blanks.

3.2.8 For instruments that inject a specified volume of sample:

3.2.8.1 Inject the volume used in a routine analytical sequence.

3.2.8.2 Analyze the first reagent blank using the same length and number of integrations and replications as is used in the routine analysis of samples.

3.2.8.3 Flush the system after each analysis according to normal operating procedures.

3.2.8.4 Repeat this procedure for the remaining reagent blanks.

3.2.9 After analyzing the blank sample, run quality control standards at CLP or laboratory-established limits. The criterion for acceptance is that analyte concentrations should be within 90% - 110% of the known value for ICP-AES, ICP-MS, GFAAS, and FAAS analyses, 80% - 120% for CVAAS (mercury).

3.2.10 Calculate the standard deviation (σ) by the following formula:

$$\sigma = \sqrt{\frac{\sum (v_1 - \bar{x})^2}{n-1}}$$

n = number of analyses performed (10)
v_i = the ith analytical value
$\bar{x}$ = average of all analytical values

3.2.11 The IDL is calculated by multiplying the standard feviation (σ) of the observed analyte concentrations by three.

IDL = 3 x σ

3.3 Determine the method detection limit (MDL).

3.3.1 Definition: The MDL is the amount of constituent that produces a signal sufficiently large that 99% (3σ) of the trials with that amount will produce a detectable signal.

3.3.2 Prepare a low level standard (LLS) for the MDL determination.

3.3.2.1 The concentration of each analyte in the LLS is determined as follows.

3.3.2.1.1 Define a range for the analyte which is no less than three times the IDL but not greater than five times the IDL.

3.3.2.1.2 Define the concentration for each analyte in the LLS as a whole number within this range which can be easily manufactured by dilution of stock standards.

3.3.2.2 Prepare a stock solution which contains the analytes interest at 100-200 times the low level standard concentrations determined in the previous section.

3.3.2.3 Prepare the LLS with ultra-pure reagents matching the acid matrix of the blank solution.

3.3.2.4 Transfer the LLS solution to seven, clean, analytical containers.

3.3.3 Analyze the low level standard.

3.3.3.1 Calibrate and run initial quality control standards according to CLP and Laboratory guidelines.

3.3.3.2 Analyze a reagent blank solution just prior to analysis of the LLS to insure that no carryover contamination exists.

3.3.3.3 Analyze the LLS. Normal injection, flush time, equilibration, number of repetitions and wash-out procedures should be adhered to for the analysis.

3.3.3.4 Repeat this procedure for each of the seven LLS replicate samples.

3.3.3.5 Final quality control standards should follow the last analysis of the LLS.

3.3.3.6 Report the concentration values in the appropriate units.

3.3.3.7 Calculate an estimated MDL as follows:

$$\text{Estimated MDL}_{\text{single day}} = t \times \sigma$$

where, t = One-sided t distribution value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom ($t \approx 3$ for seven replicates).

and, σ = standard deviation of the seven replicate analyses using n-1 degrees of freedom.

3.3.3.8 Analyze the LLS according to 13.3.3.3 on three non-consecutive days and within a one month period.

3.3.3.9 RDLs will be determined biannually - during the months of January and June.

3.3.3.10 Calculate the final MDL by averaging the three estimated MDL determinations.

$$\text{Final MDL} = \frac{\text{MDL}_{\text{day1}} \pm \text{MDL}_{\text{day2}} \pm \text{MDL}_{\text{day3}}}{3}$$

3.4 Establish the reliable detection level (RDL).

3.4.1 Definition: The RDL is a practical amount of constituent above the MDL which provides a reasonable level of detection to avoid false identifications of analytes at the method detection limit.

3.4.2 The RDL is established as the reportable level of detection and, as a policy decision, will be determined by the EPA Metals Team Leader.

3.4.3 The RDL is reported with two significant figures.

3.5 Determine the practical quantitation level (PQL).

3.5.1 Definition: The PQL is the experimentally determined lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operation conditions.

3.5.2 Begin by estimating the PQL at twice the RDL.

3.5.2.1 Prepare a PQL stock solution with the constituent concentrations at 100 to 200 times the estimated PQL.

3.5.2.2 Prepare the PQL working solution (analytes at the estimated PQL) with ultra-pure reagents matching the acid matrix of the blank solution.

3.5.2.3 Transfer the PQL solution to ten, clean, analytical sample containers.

3.5.3 Analyze the PQL solution.

3.5.3.1 Calibrate and run initial quality control standards according to CLP and Laboratory guidelines.

3.5.3.2 Analyze a reagent blank sample just prior to analysis of the PQL sample to insure that no carryover contamination exists.

3.5.3.3 Analyze the PQL sample. Normal injection, flush time, equilibration, number of repetitions and wash-out procedures should be adhered to for the analysis.

3.5.3.4 Repeat this procedure for each of the ten PQL replicate samples.

3.5.3.5 Final quality control standards should follow the last analysis of the PQL sample.

3.5.3.6 Report the concentration values in the appropriate units.

3.5.3.7 Calculate the mean ($\bar{x}$), standard deviation (σ) and percent relative standard deviation (%RSD) of the ten ananytical results for each analyte.

$$\bar{x} = \frac{x_1 + x_2 + x_i \ldots x_{10}}{10}$$

$$\sigma = \sqrt{\frac{\sum (v_i - \bar{x})^2}{n-1}}$$

$$\%RSD = \frac{\sigma}{\bar{x}} x100$$

(See 3.2.10 for definitions of variables)

3.5.3.8 A valid PQL is established if the % RSD is less than or equal to 10% and the mean recovery of the analyte is within 90 - 110% of the true value.

3.5.3.8.1 If the limits of precision and accuracy are achieved in the first trial, the level of the PQL may have been overestimated and levels lower than twice the RDL should be evaluated. This also suggests that the RDL was overestimated and requires additional inspection.

3.5.3.9 Repeat sections 3.5.2 - 3.5.3 at three, four, five, etc. times the RDL until all analytes of interest demonstrate ≤10 %RSD and the mean recovery of the analyte is within 90 - 110% of the true value.

4.0 References

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